



Hydrogen Embrittlement of 316/316L Stainless Steel

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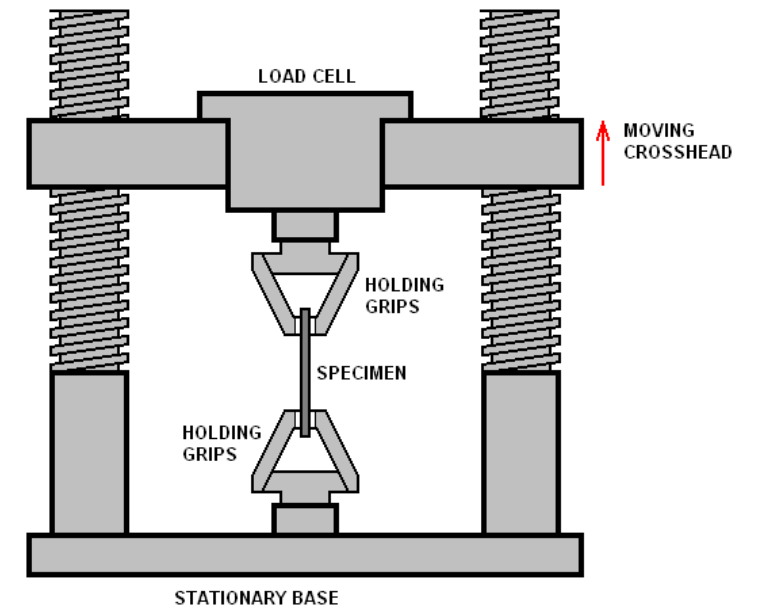
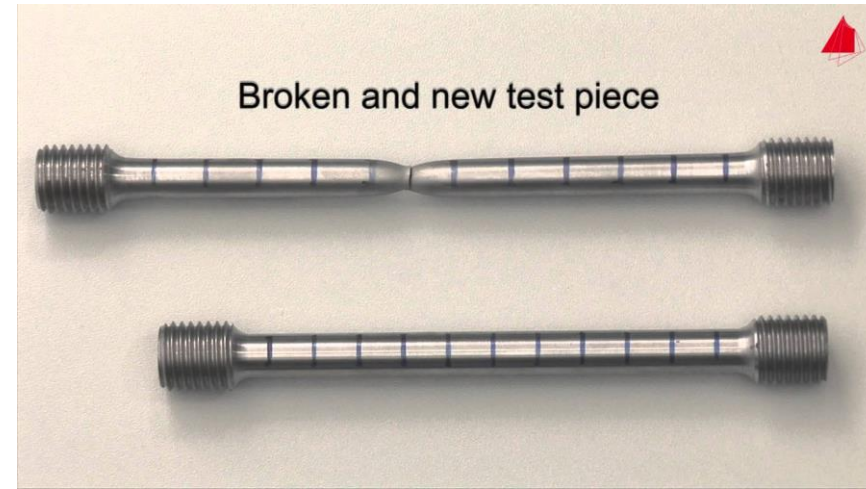
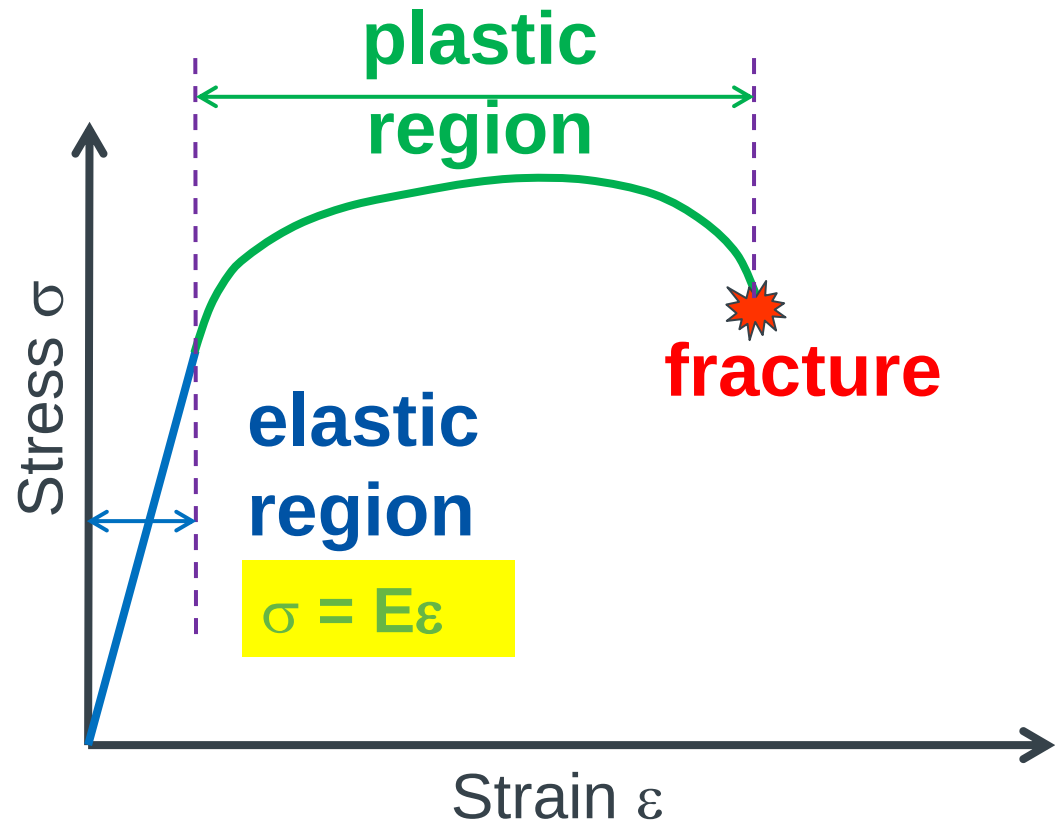
Swagelok®

Overview

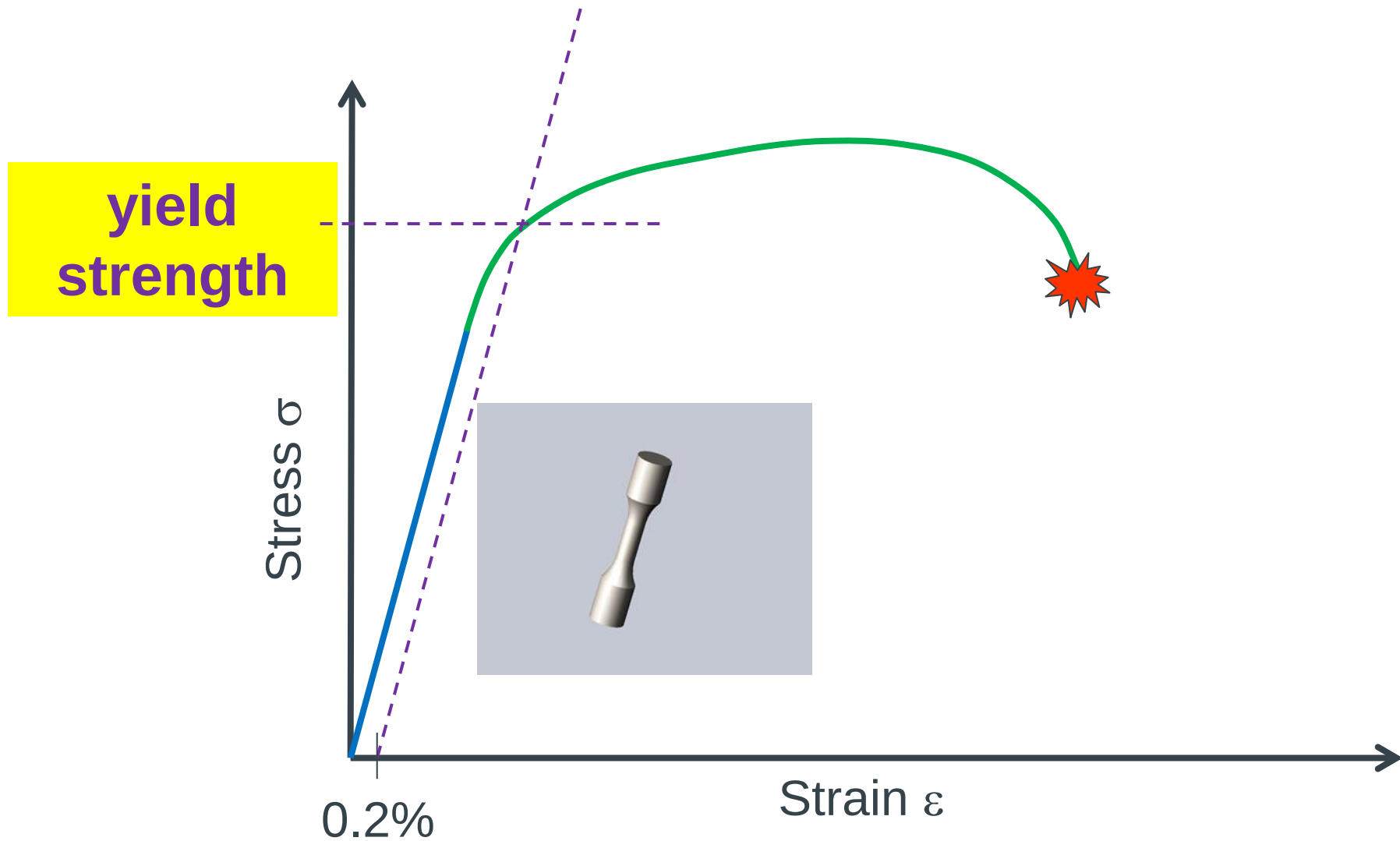
- Review of mechanical properties and fatigue behavior
- Hydrogen embrittlement: effect of hydrogen on
 - Yield and tensile strength
 - Elongation and reduction of area
 - Fatigue strength and fatigue life
- Pressure cycling and integrity of fluid system components
 - Effect of hydrogen
- Requirements for Ni-content
- Conclusions

Stress-strain curve

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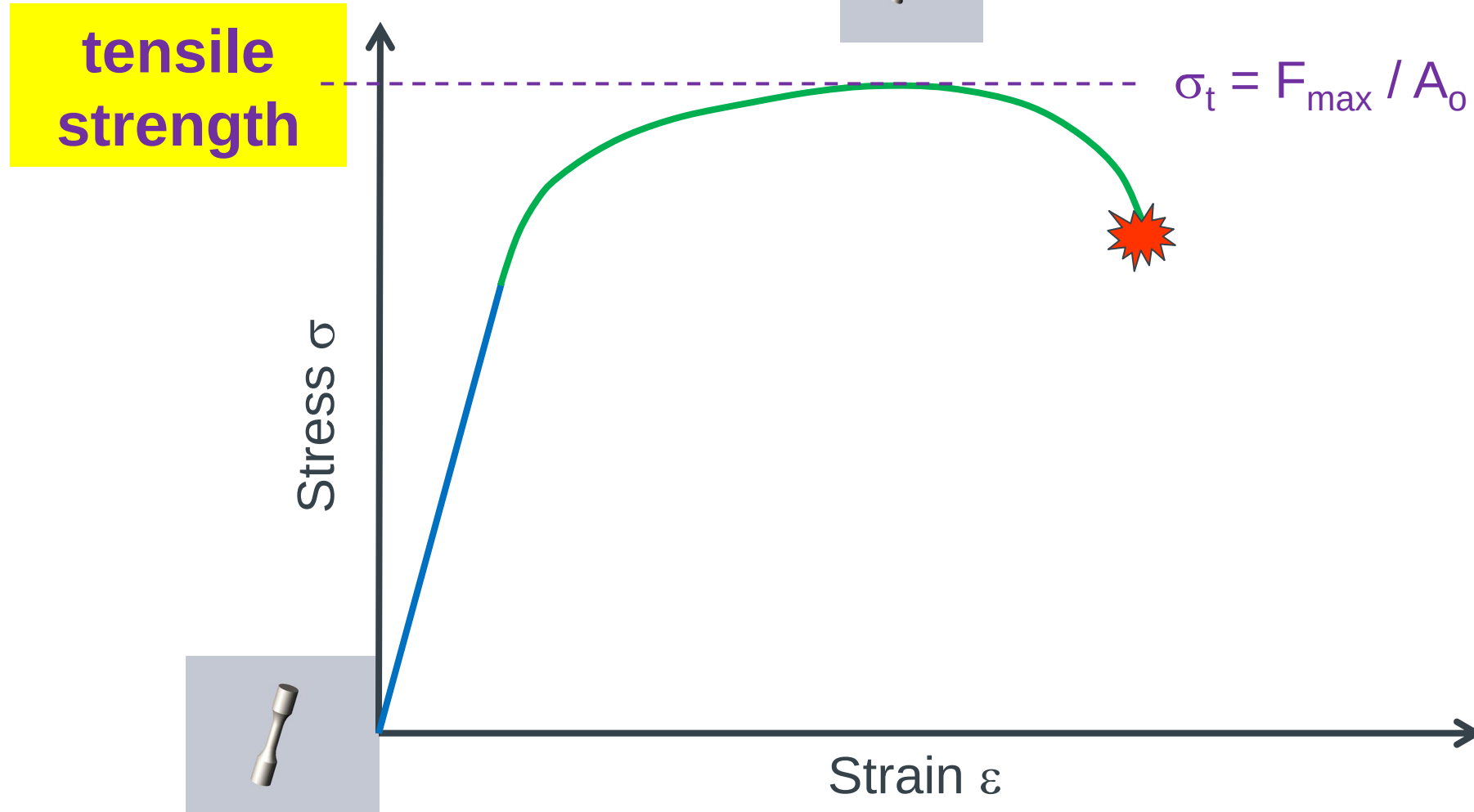


Yield strength



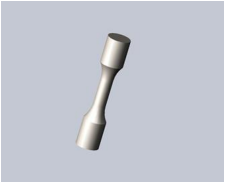
Tensile strength

Swagelok

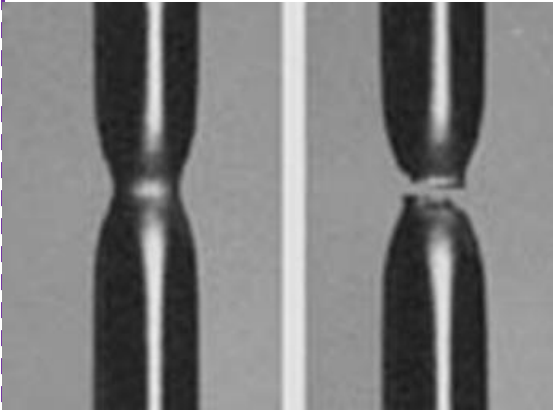
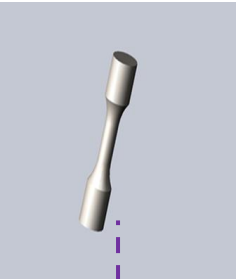
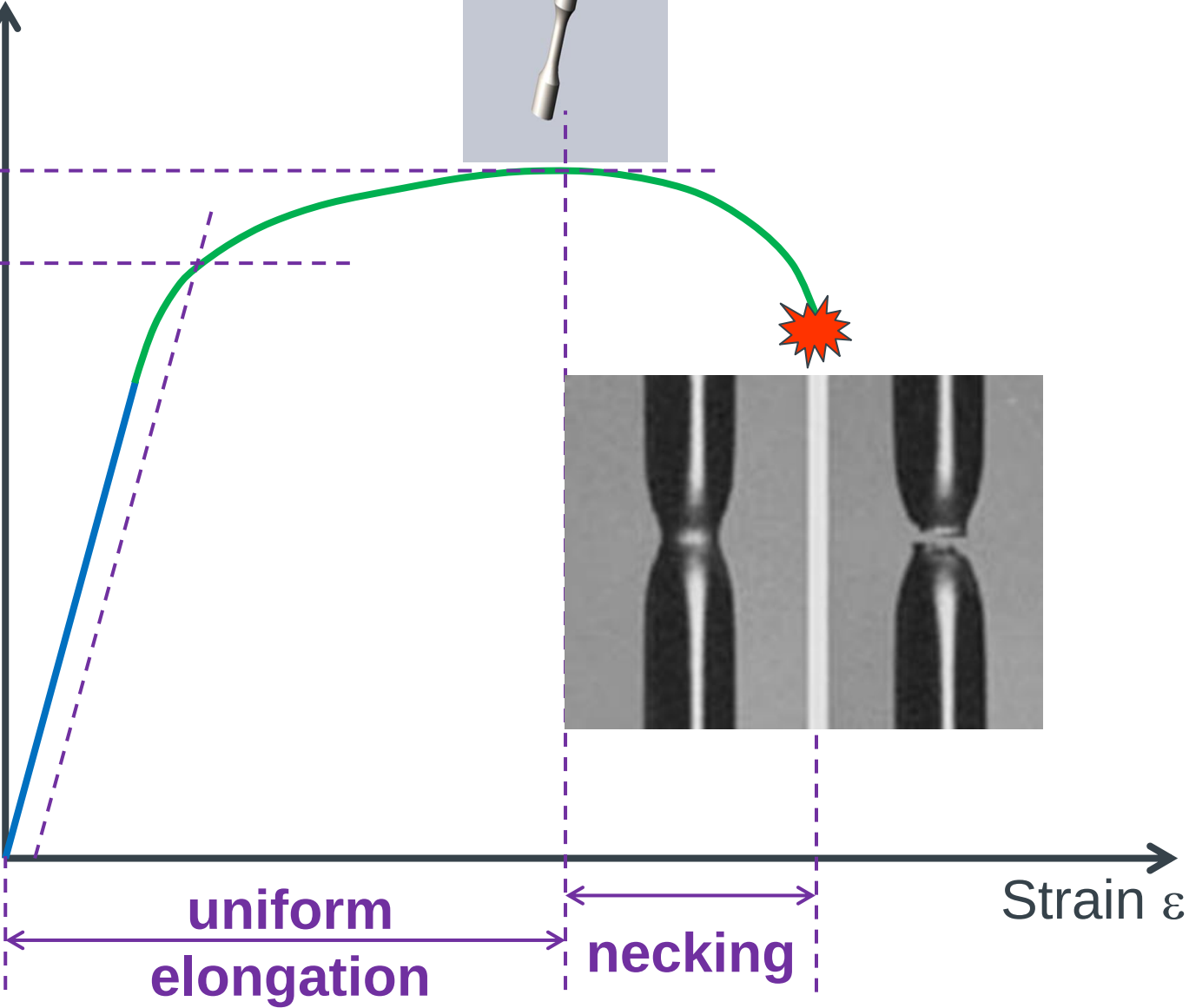


Elongation

tensile strength
yield strength



Stress σ

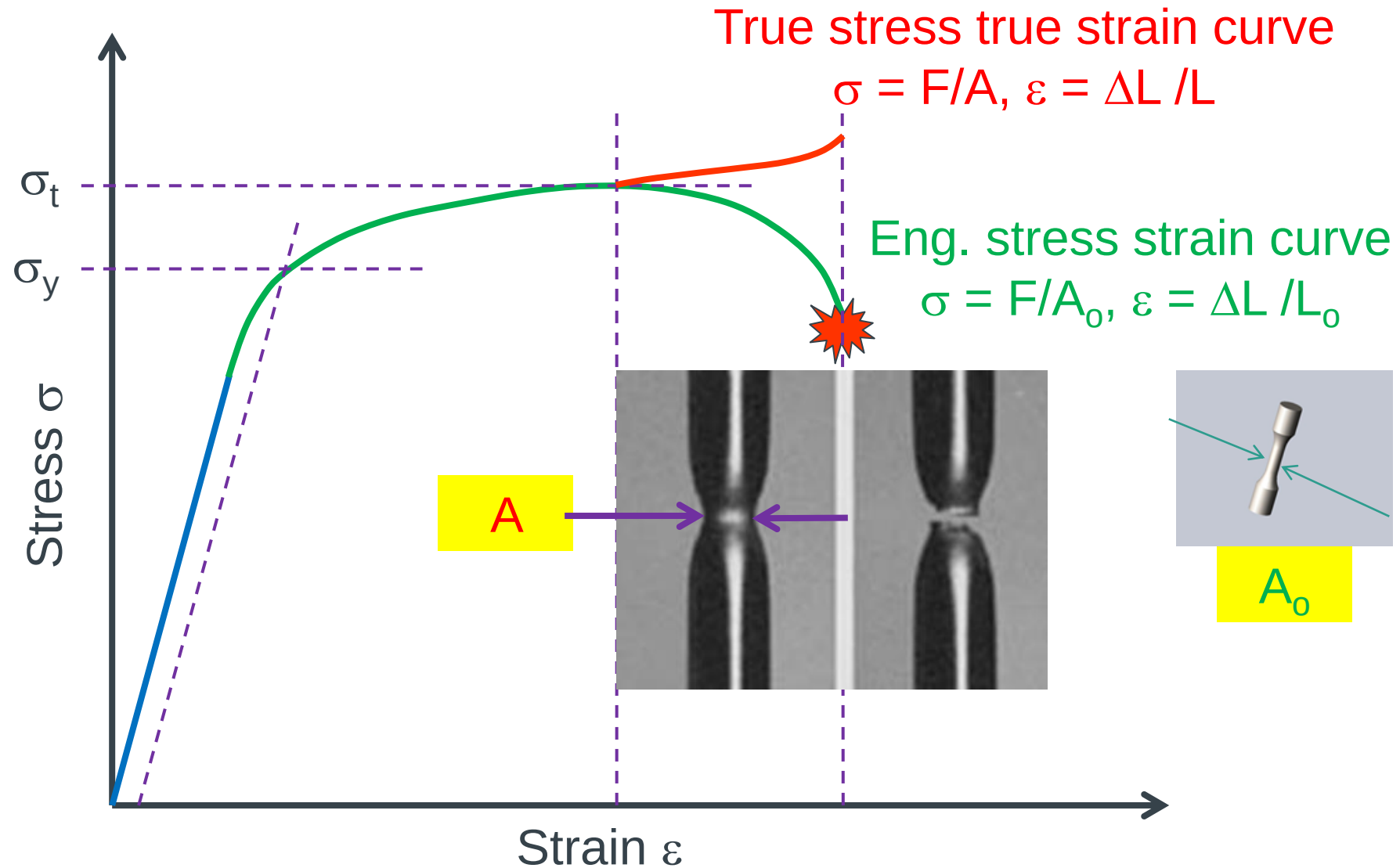


uniform
elongation

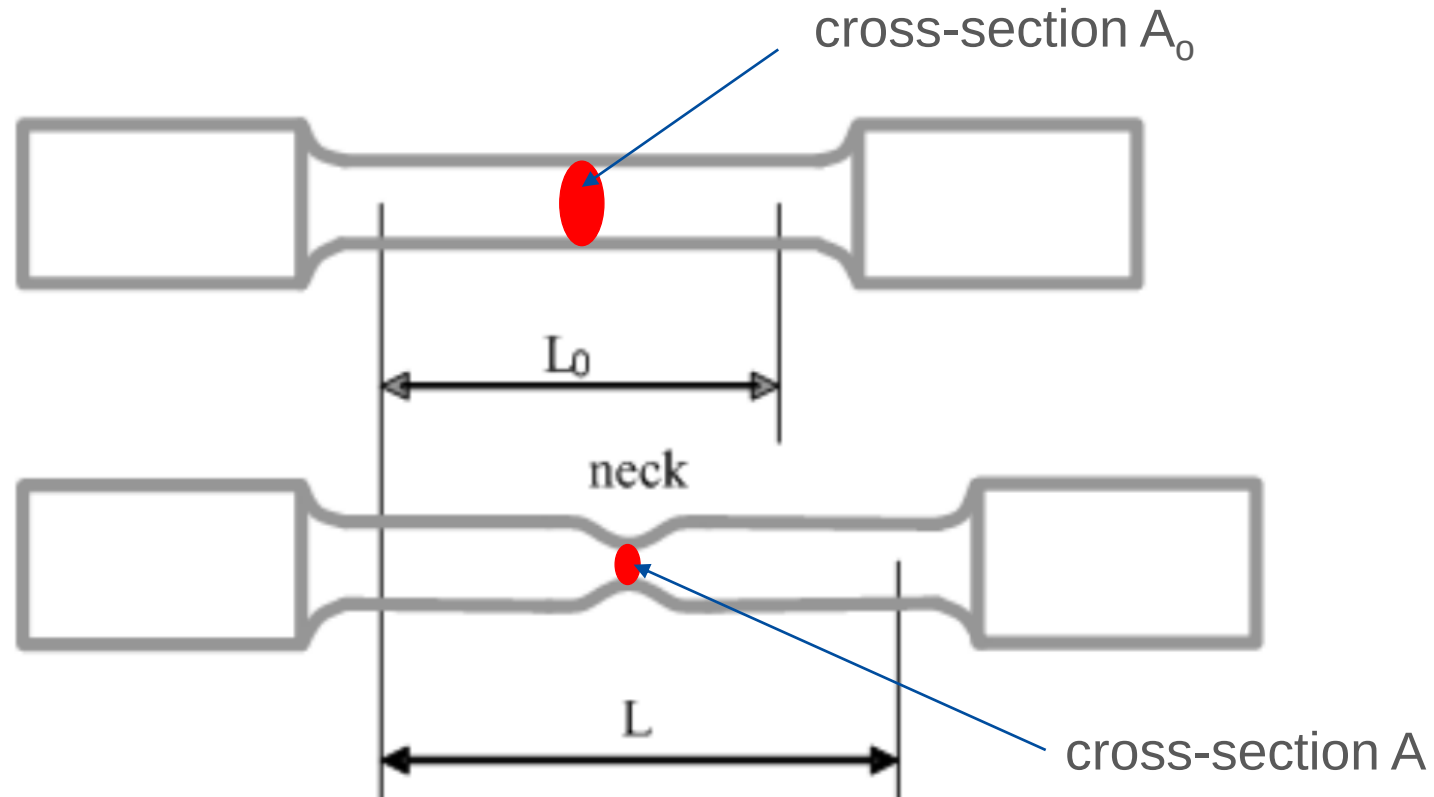
necking

Strain ϵ

True stress true strain behavior



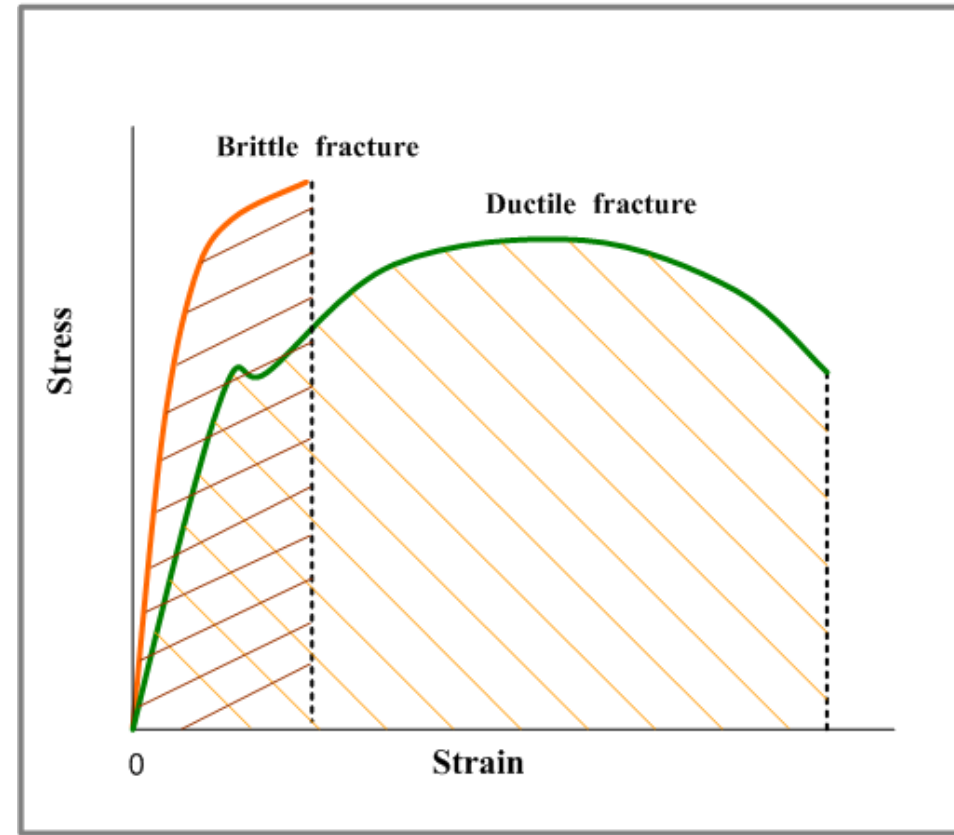
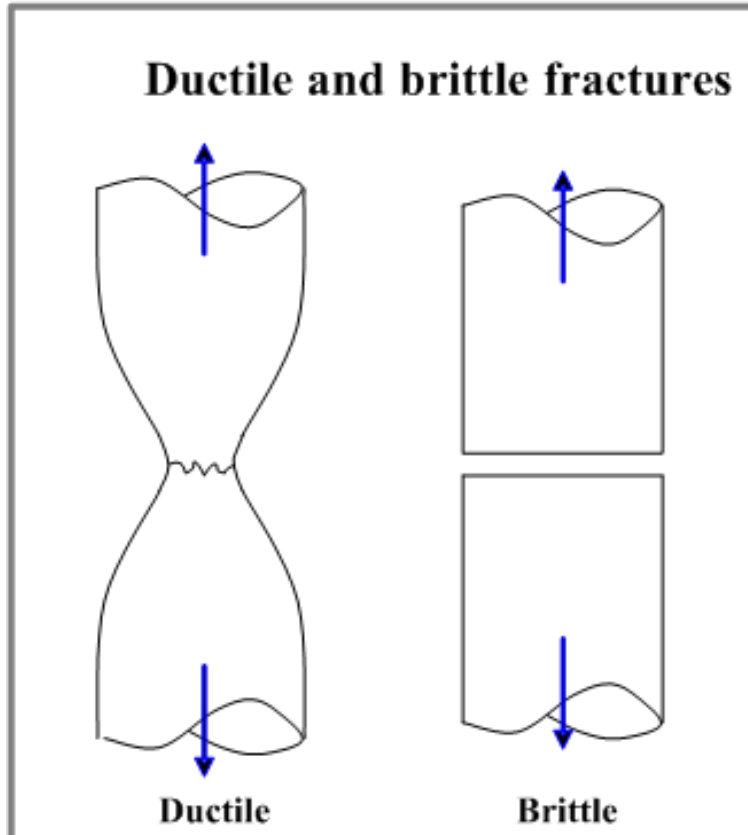
Measures of ductility



$$\text{Strain-to-failure } \epsilon_f = (L - L_0) / L_0$$

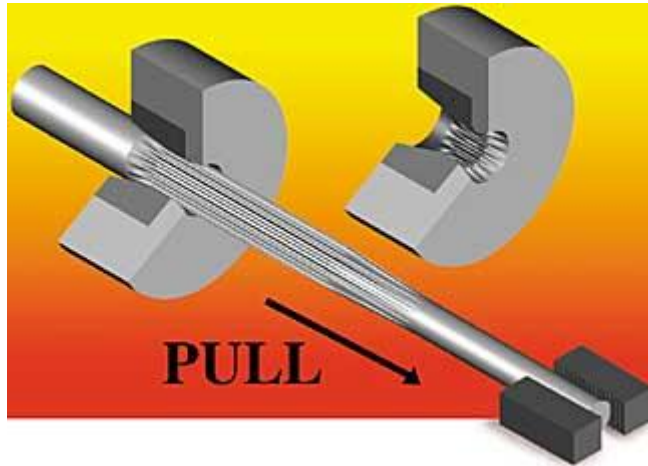
$$\text{Reduction of area } RA = (A_0 - A) / A_0$$

Fracture

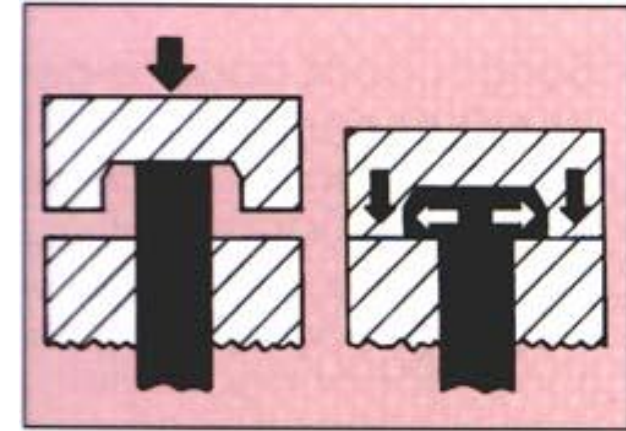


Fracture energy:
 $E = \int \sigma d\epsilon$
Area under stress-strain curve

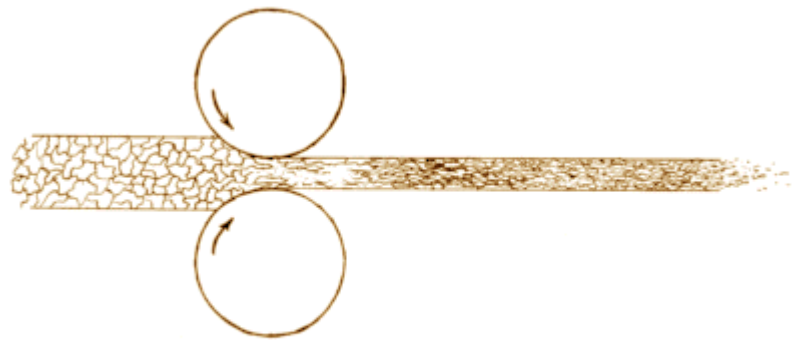
Strain-hardening



cold drawing



cold heading



cold rolling

Metal fatigue

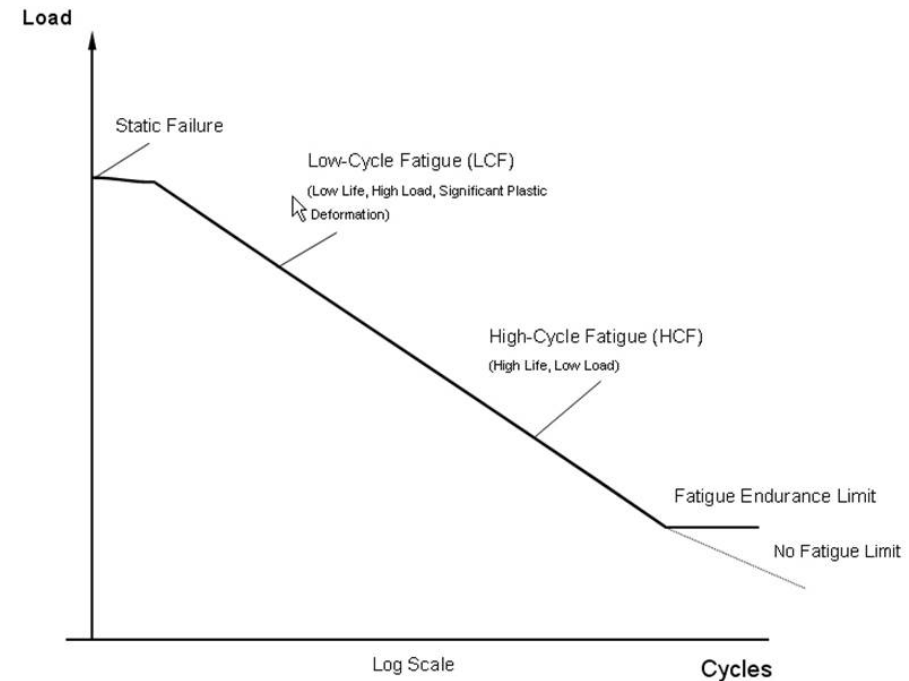
- Weakening of a material caused by cyclic loading
- Causes progressive localized structural damage
- Leads to initiation of crack(s)
 - each loading cycle causes the crack to grow by a very small distance
 - crack grows until it reaches a critical size
 - complete fracture of the structure occurs



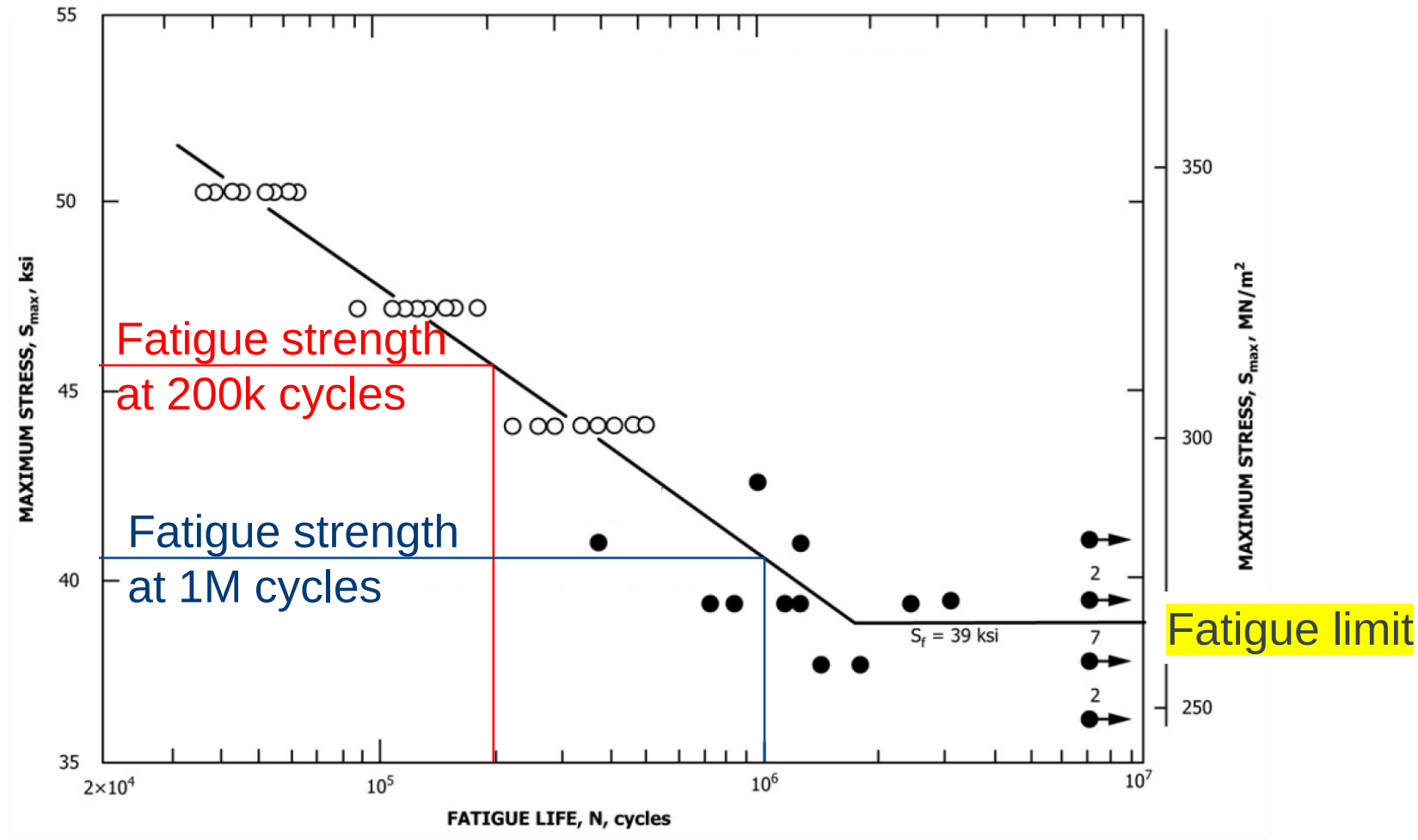
<https://hill-engineering.com/our-work/fracture-surfaces-evaluation/>

Fatigue testing

- Applying a cyclic load to a specimen or an actual part
 - generate fatigue life and crack growth data
 - identify critical locations which can lead to fatigue failure
 - demonstrate the safety of a structure susceptible to fatigue



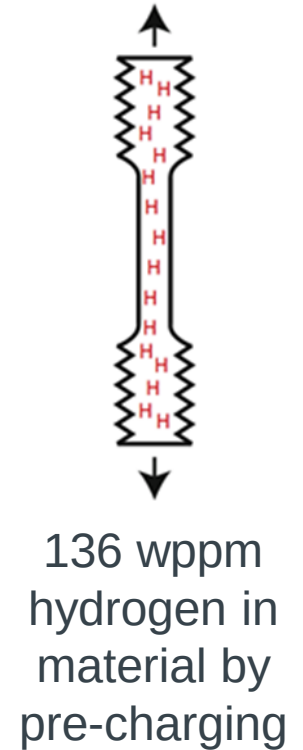
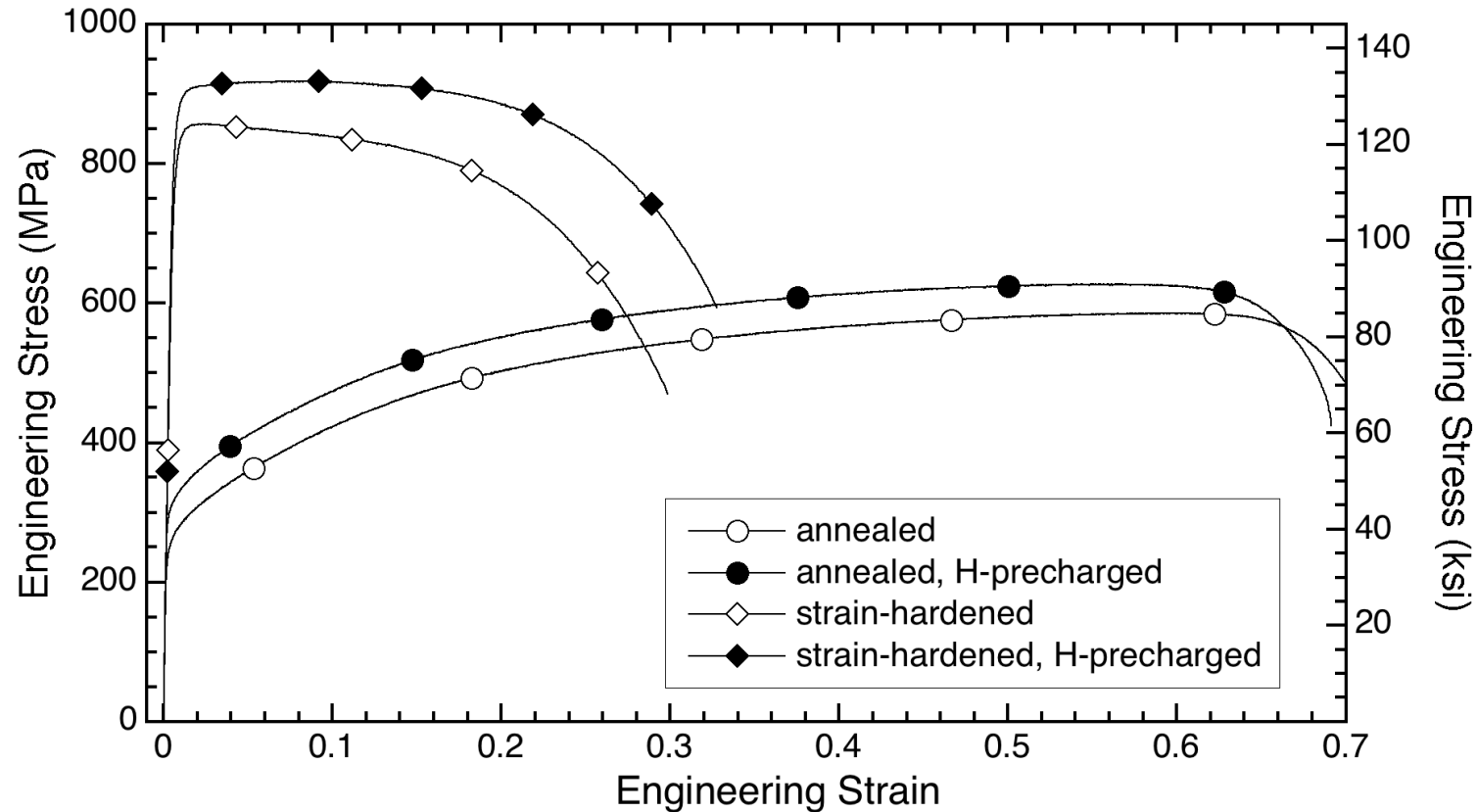
Fatigue-life (S-N) curve



Effect of hydrogen on metals

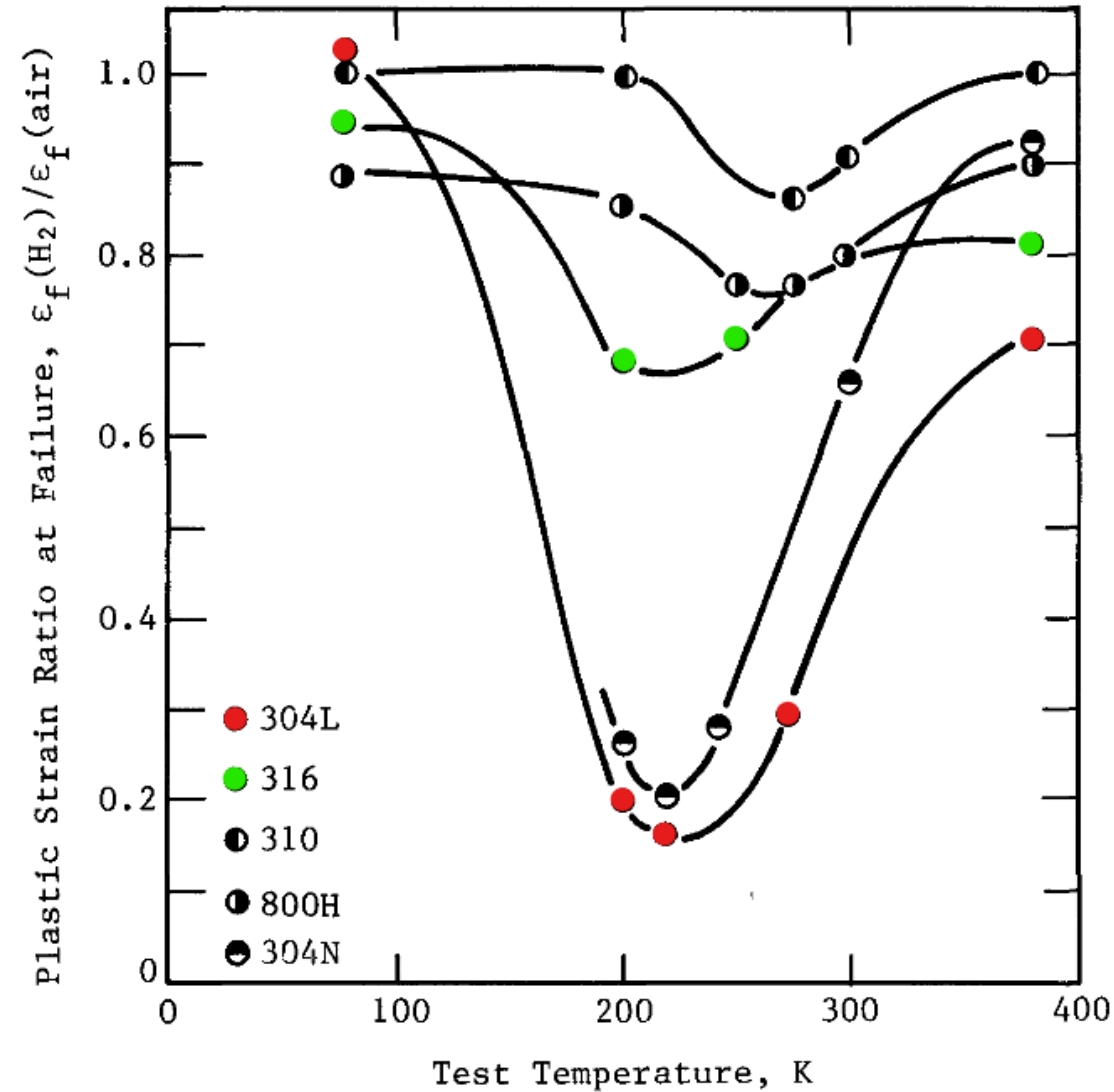
- Key questions
 - How does embrittlement happen?
 - H_2 adsorption $\rightarrow$ H-atoms $\rightarrow$ diffusion into material
 - How are different materials affected?
 - 15 years of testing Swagelok materials by national laboratories
 - Can 316 stainless steel be used safely?
 - Depends on quality, product design, operating conditions
- H_2 can cause change of properties & behavior of metals
 - Strength: yield strength and ultimate tensile strength
 - Ductility: strain-to-failure and reduction of area
 - Fatigue behavior: cycle life and fatigue limit

Stress-strain curves of 316/316L

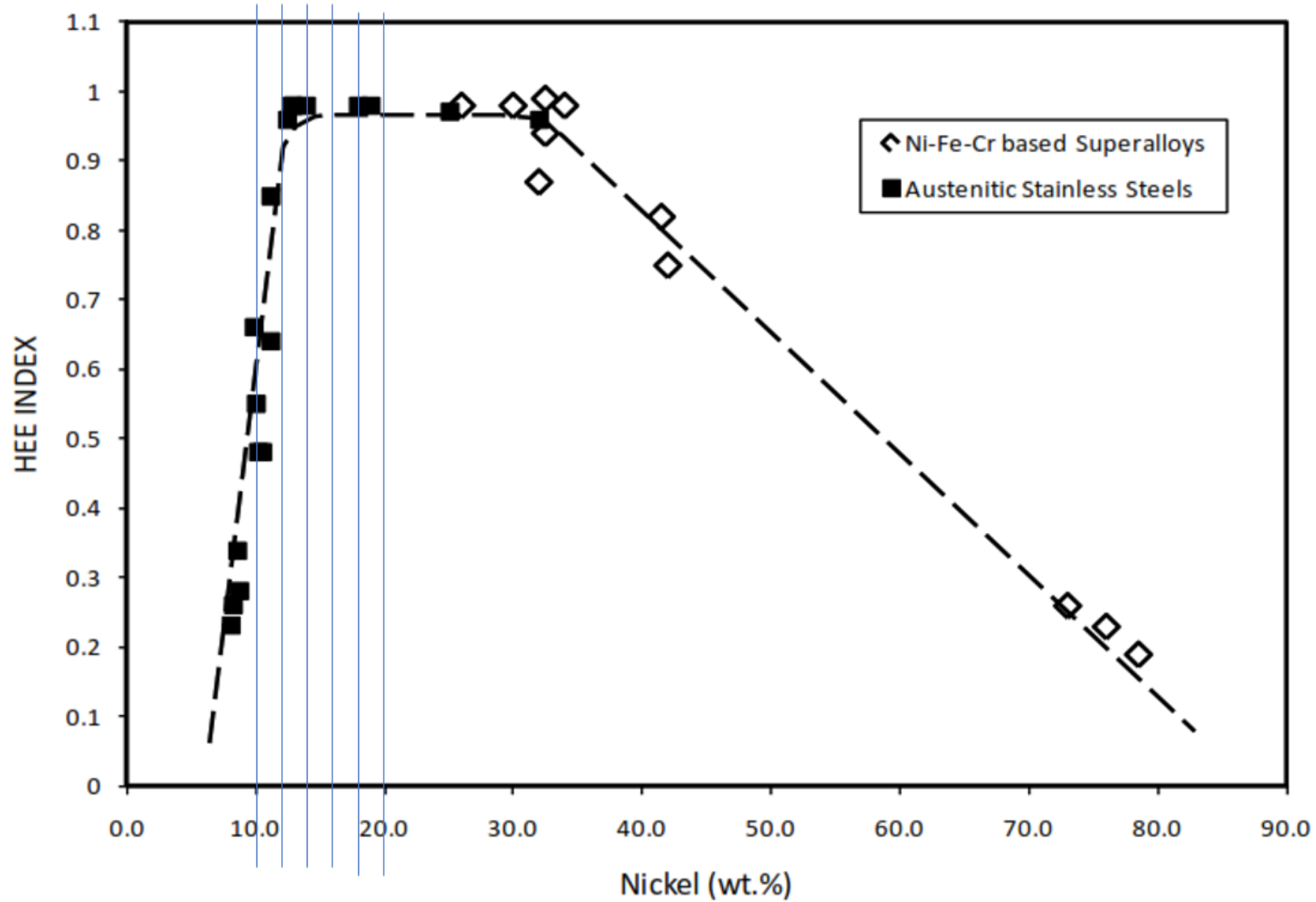


- Hydrogen affects mechanical properties of 316/316L
 - Increases yield strength and tensile strength
 - Does not affect strain-to-failure (ductility)

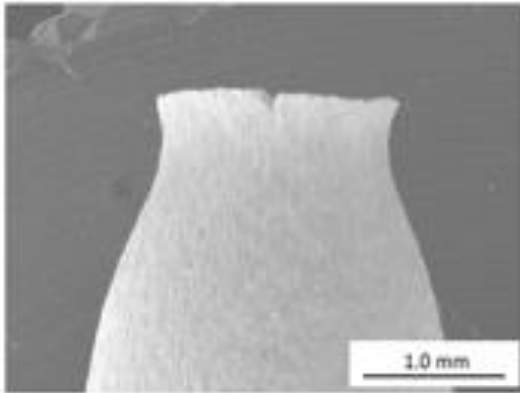
Elongation in air & H₂ as f(T)



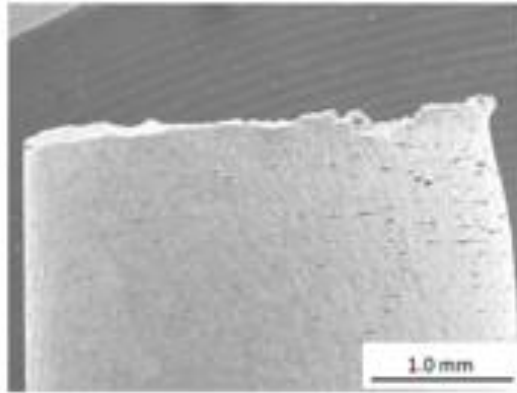
Importance of nickel content



HE of 304 and 316 SS

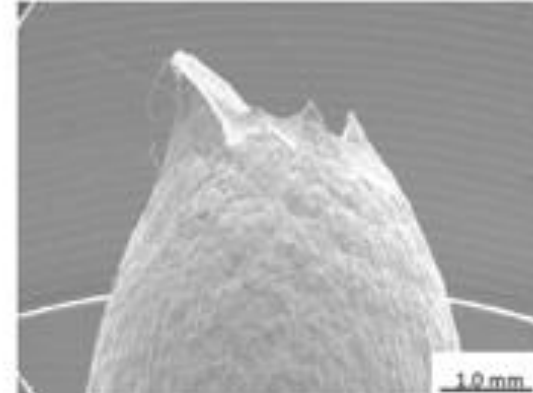


In air, $\phi_{\text{air}} = 83.3 \%$

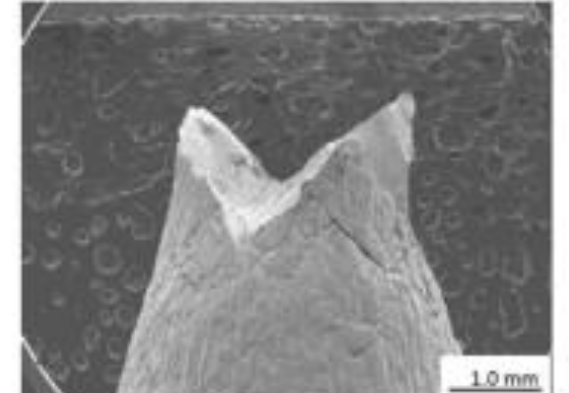


In 83 MPa H₂, $\phi_{\text{H}} = 38.3 \%$

304 SS (18.16 %Cr, 8.15% Ni)



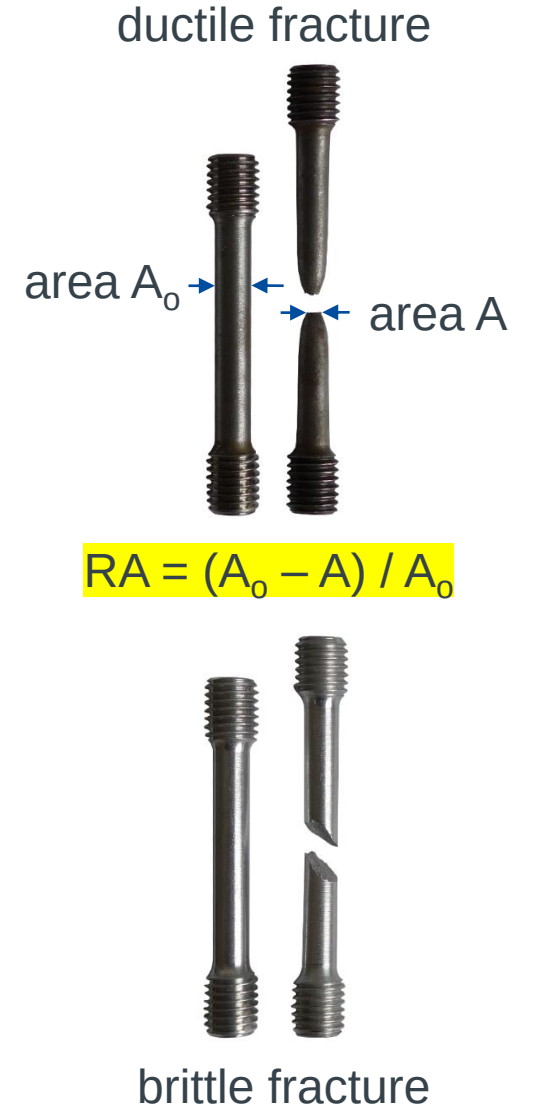
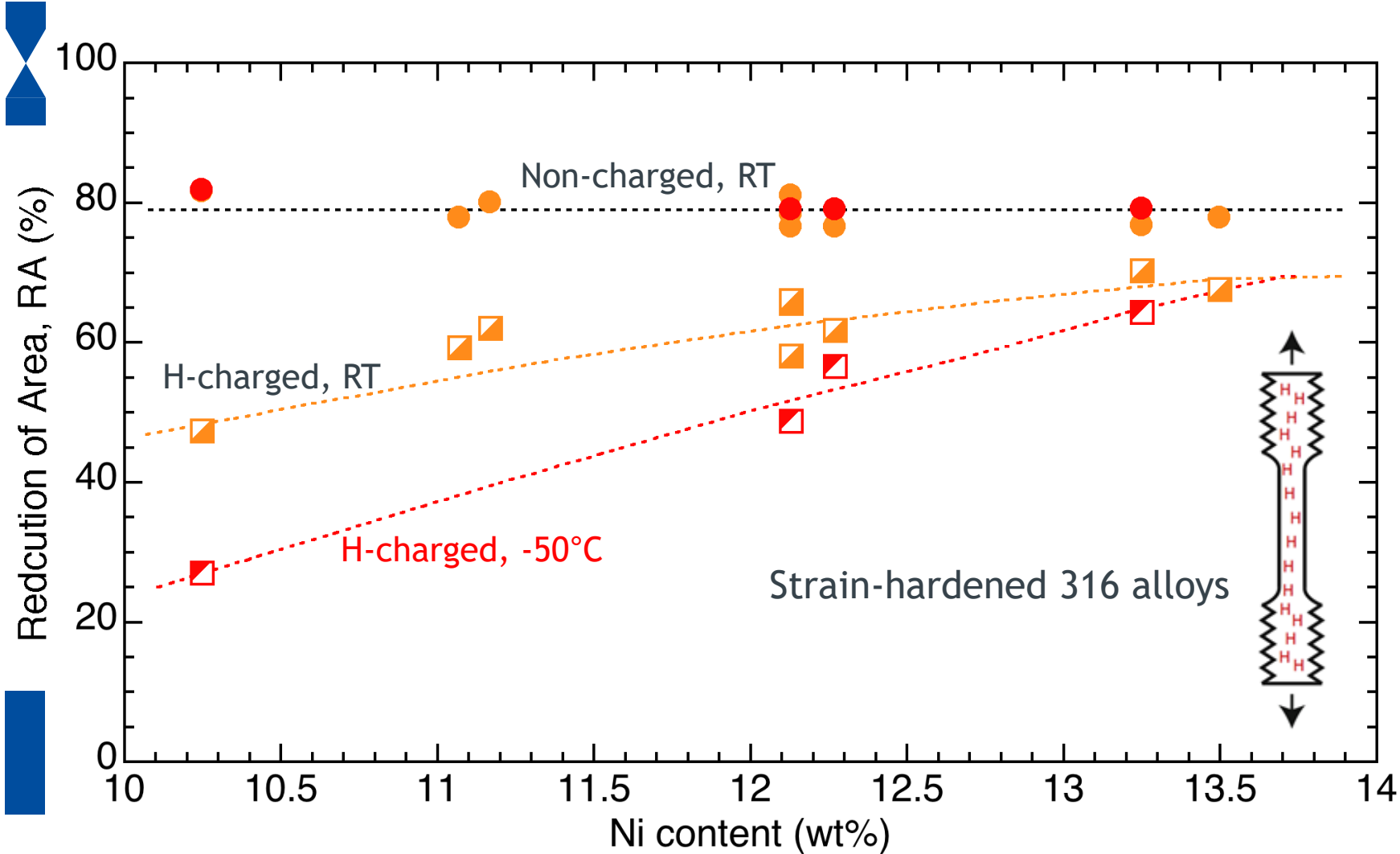
In air, $\phi_{\text{air}} = 87.0 \%$



In 78 MPa H₂, $\phi_{\text{H}} = 82\%$

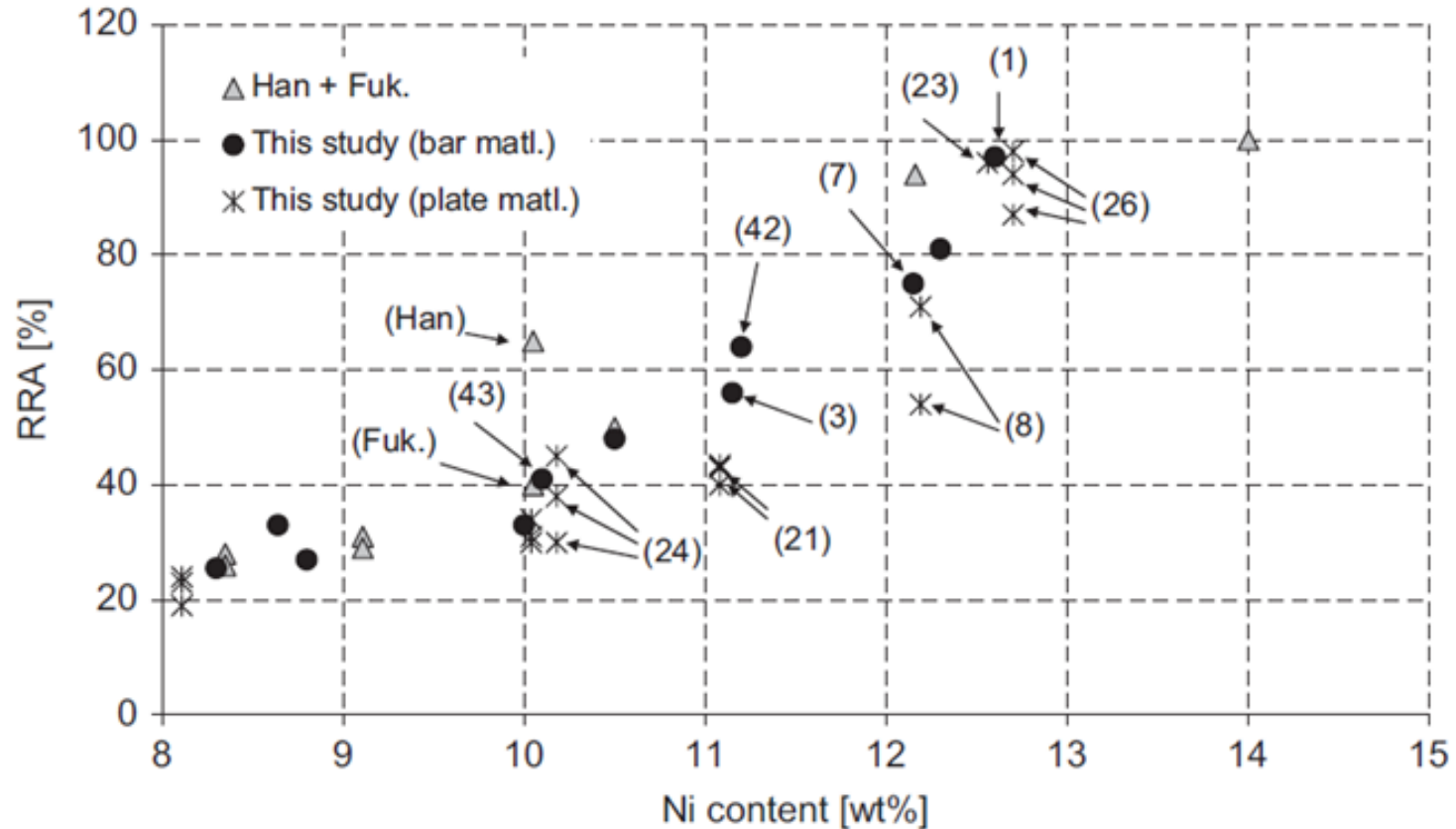
316 SS (17.64 %Cr, 12.22 %Ni)

Effect of Ni-content and temperature on RA



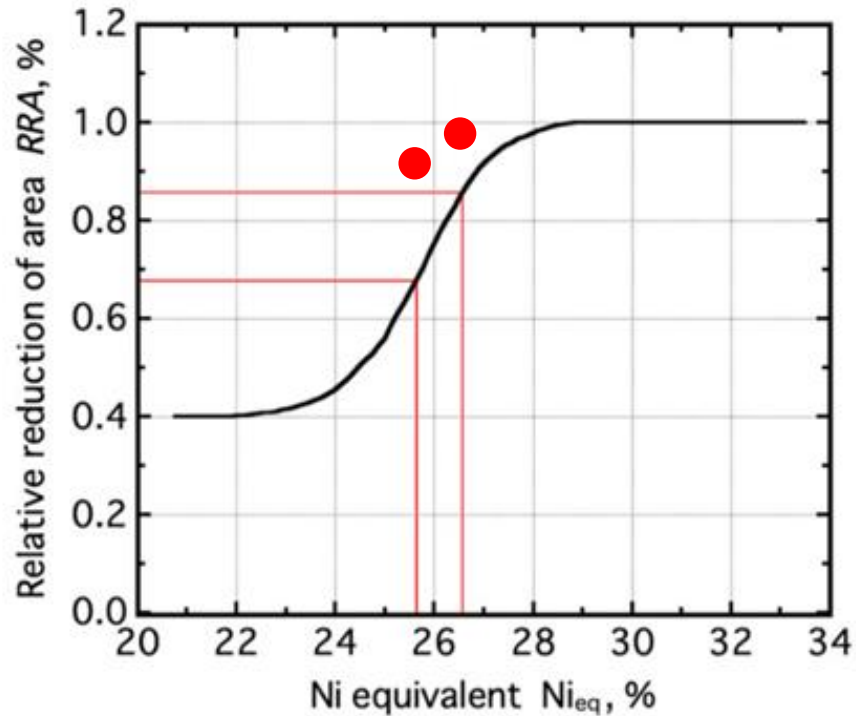
RRA versus Ni-content

RA (H₂) / RA (air)

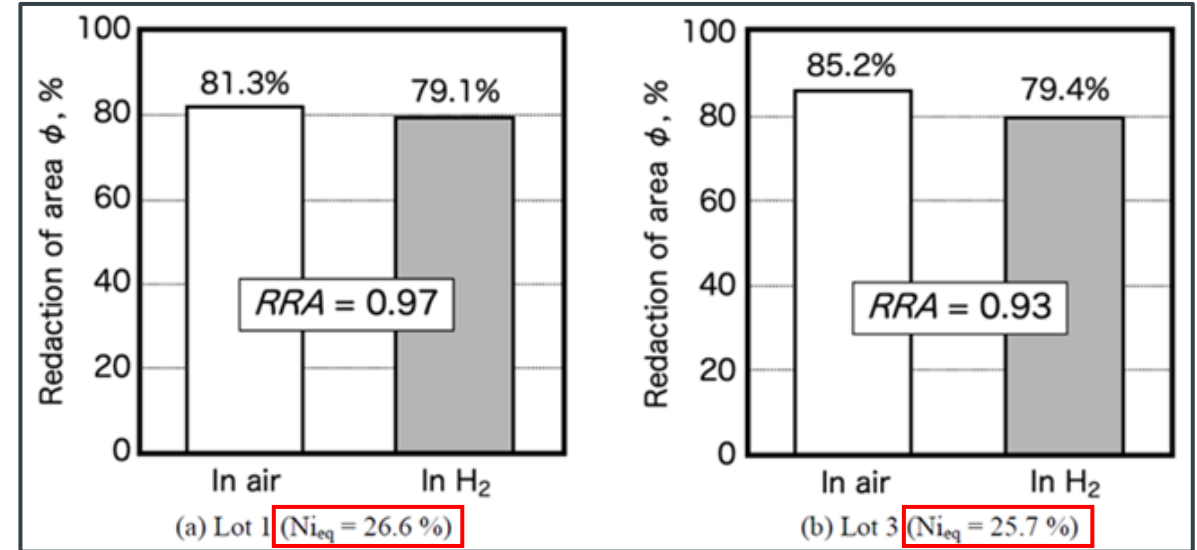


Thorsten Michler, Joerg Naumann, Hydrogen environment embrittlement of austenitic stainless steels at low temperatures, Int. J. Hydrogen Energy, 33 21 11 – 21 (2008)

RRA versus Ni-eq



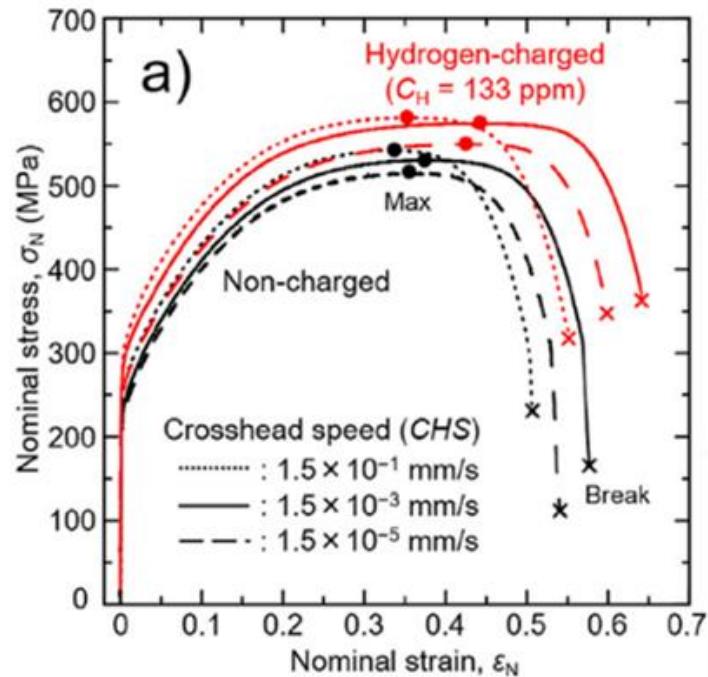
Yamada, T., Kobayashi, H., Materials selection standard for hydrogen station equipment, J. of the High-Pressure Gas Safety Institute of Japan, 49, 885-893, (2012)



$$\text{Ni-eq} = \text{Ni} + 12.6\text{C} + 1.05\text{Mn} + 0.65\text{Cr} + 0.98\text{Mo} + 0.35\text{Si}$$

Akira Ueno, Guenec Benjamin, Effect of high-pressure H gas on tensile and fatigue properties of stainless steel SUS316L by means of the internal high-pressure H gas method, Procedia Structural Integrity 19 494–503 (2019)

RRA for alloy with Ni-eq

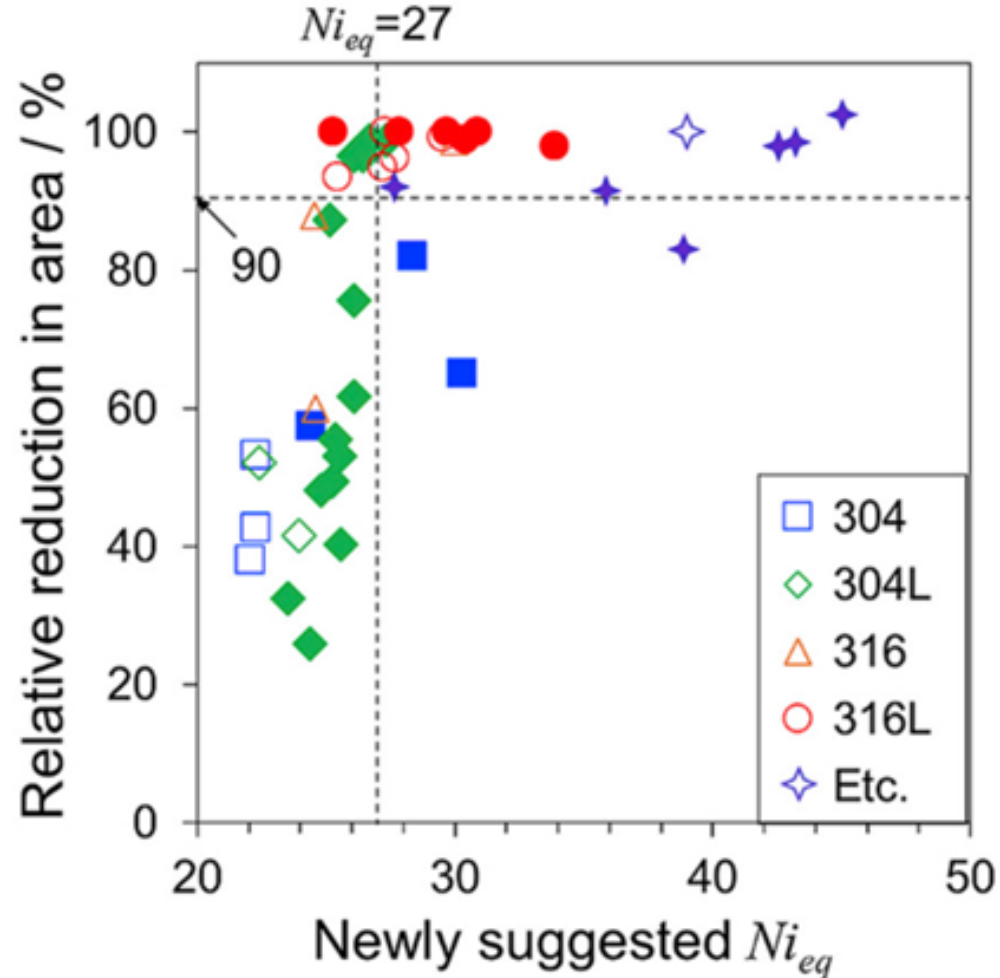


- 310 stainless steel
- Ni-eq 36.3
- RRA = 92.5

Fe	Cr	Ni	Mn	Mo	N	C	Si	S	P	Ni-eq
bal.	24.21	19.07	1.06	0	0	0.02	0.30	0.001	0.028	36.3

Yuhei Ogawa, Hyuga Hosoi, Kaneaki Tsuzaki, Timothée Redarce, Osamu Takakuwa, Hisao Matsunaga, Hydrogen, as an alloying element, enables a greater strength-ductility balance in an Fe-Cr-Ni-based, stable austenitic stainless steel, Acta Materialia 199, 181–192 (2020)

Minimum Ni-eq

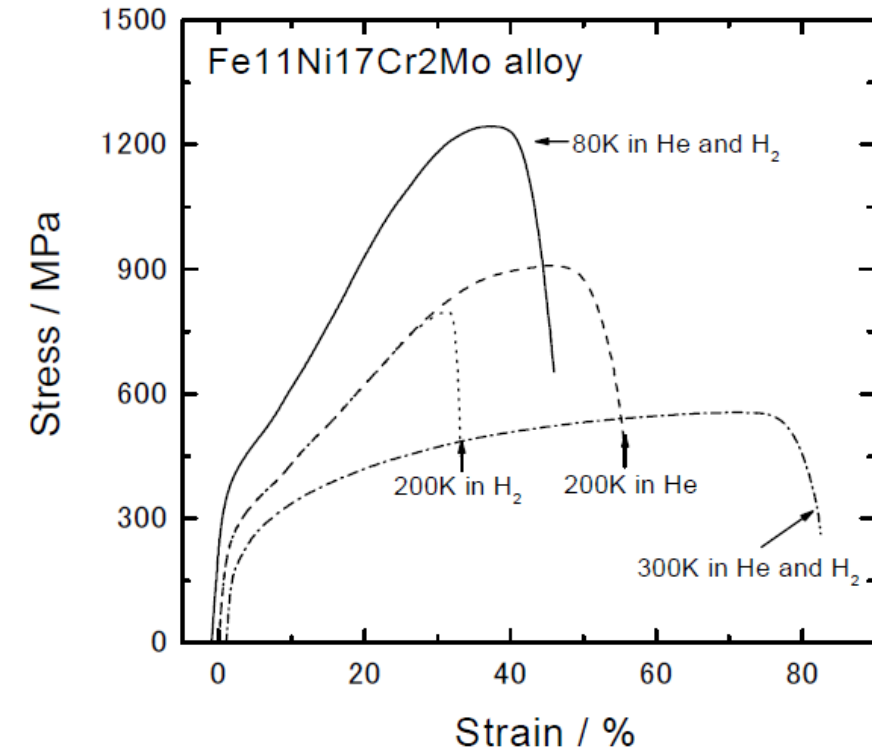
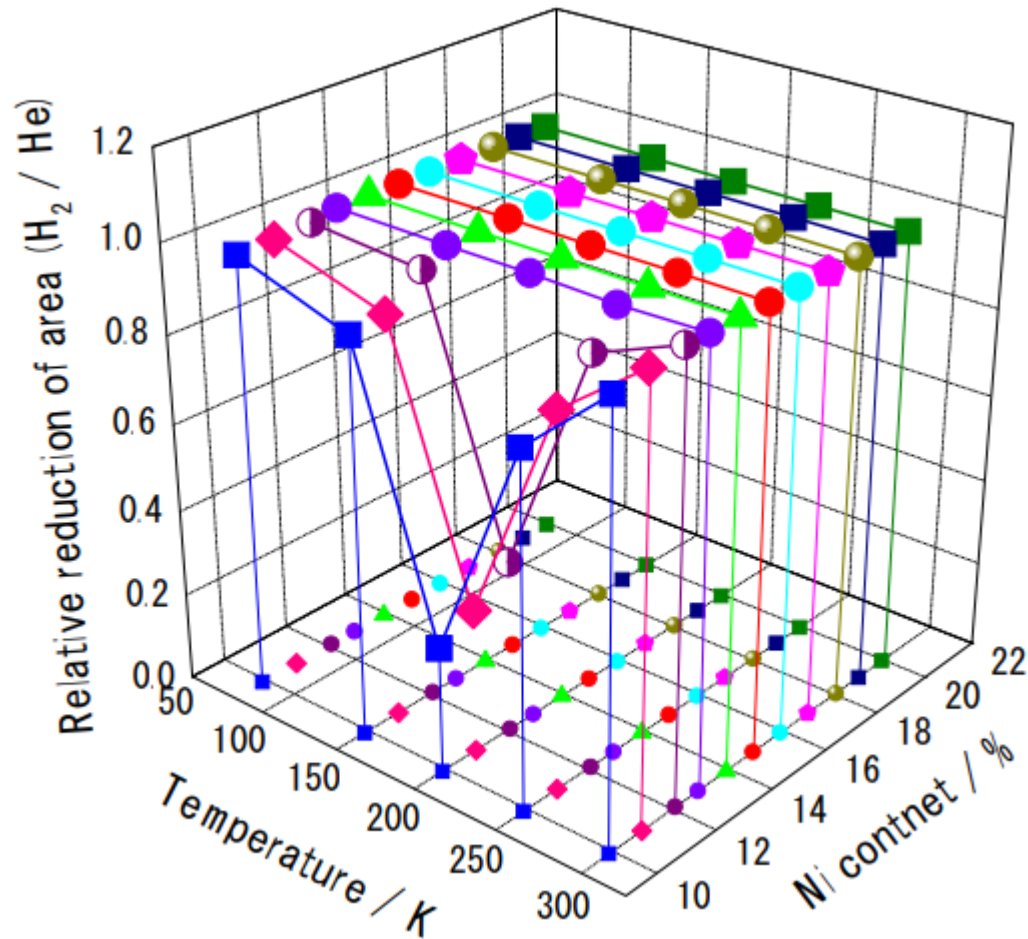


$$Ni_{eq} = Ni + 12.6C + 1.05Mn + 0.65Cr + 0.98Mo + 0.35Si$$

Jee-Hyun Kang, Han-Seop Noh, Kwang-Min Kim, Soop-Chan Lee, Sung-Jon Kim, Modified Ni equivalent for evaluating hydrogen susceptibility of Cr-Ni based austenitic stainless steels, Journal of Alloys and Compounds, Vol. 696, No. 5, 869 – 874 (2017)

Minimum Ni-eq

$$\text{Ni-eq} = \text{Ni} + 12.6\text{C} + 1.05\text{Mn} + 0.65\text{Cr} + 0.98\text{Mo} + 0.35\text{Si}$$



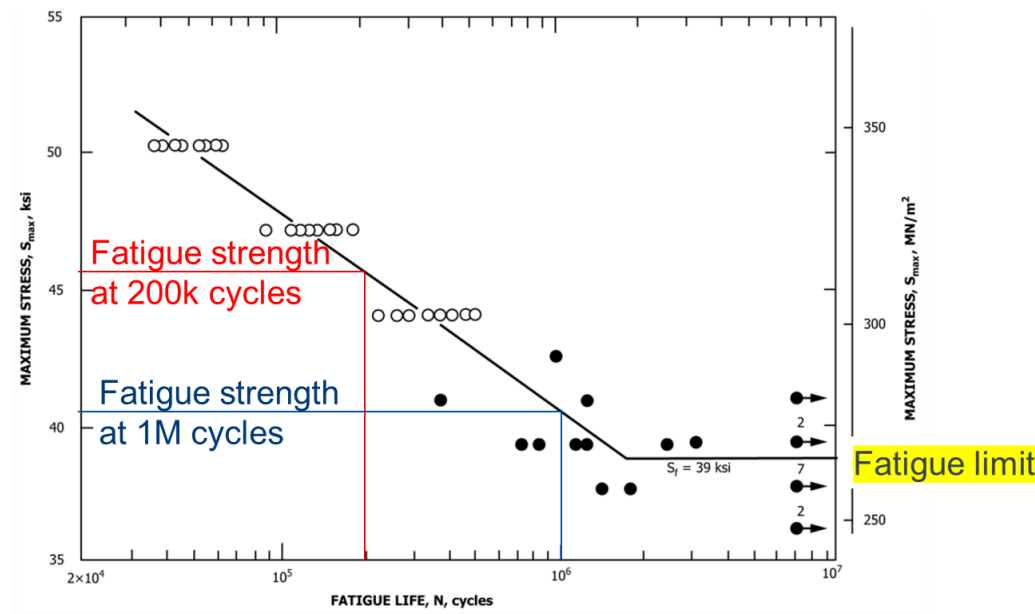
EFFECT OF NICKEL EQUIVALENT ON HYDROGEN ENVIRONMENT EMBRITTLEMENT OF AUSTENITIC STAINLESS STEELS AT LOW TEMPERATURES, L. Zhang, M. Wen, M. Imade, S. Fukuyama and K. Yokogawa, Volume 56, Issue 14, pp. 3414 – 3412 (2008).

Is RRA a useful predictor of product performance?

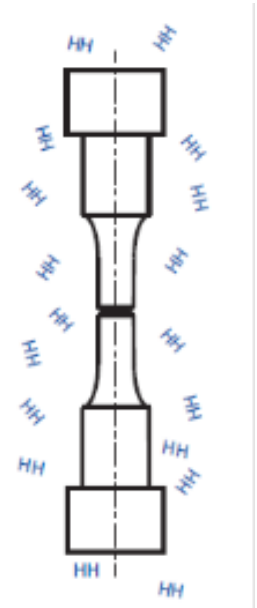
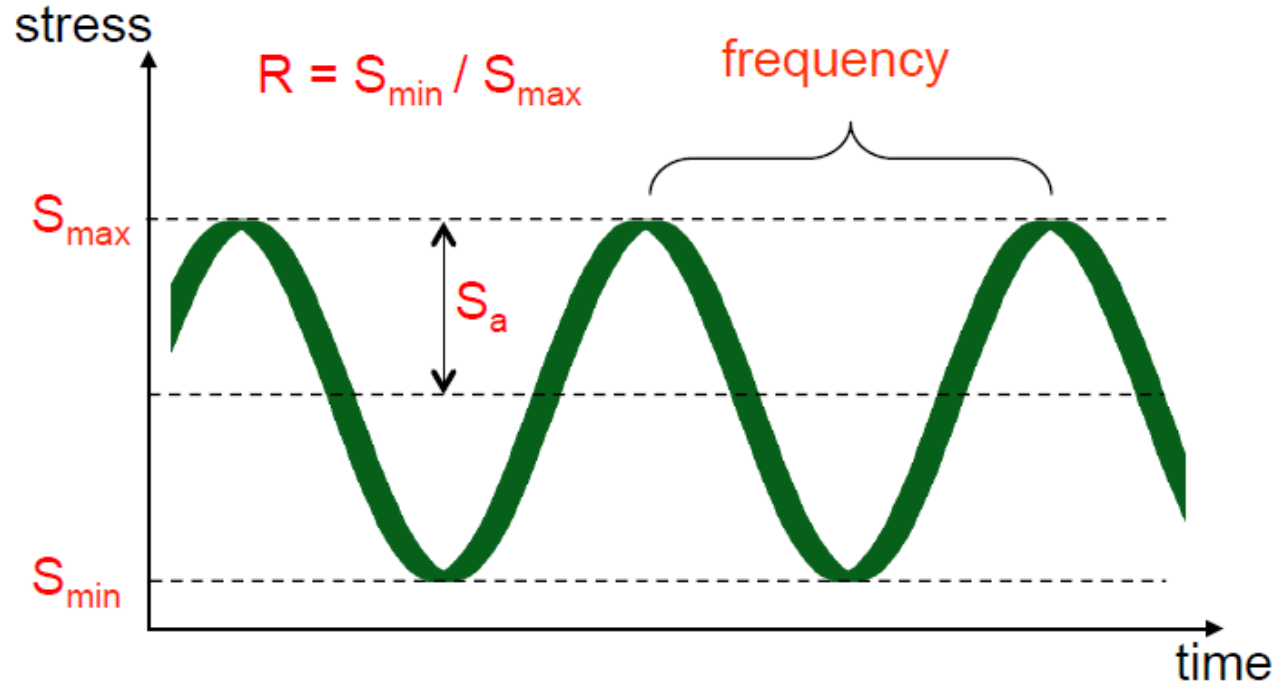
- Necking of occurs after tensile sample reaches tensile strength
- In actual use, pressurized components deform elastically only
- Microplastic deformation of material possible (at “crack tip”)
- Microplastic deformations can accumulate during pressure cycling
 - Localized strain-hardening
 - Nucleation and growth of fatigue crack
- When RRA is “low”, H_2 reduces the fatigue life
 - Occurs at stresses above a material’s fatigue limit
- Conclusion: focus on fatigue behavior of material, not on RRA

Component pressure-cycled with H₂

- What minimum stress $S_{\min}$ and maximum stress $S_{\max}$ will the component will see?
- What is the expected fatigue life of the component?
 - If infinite: Does hydrogen affect the fatigue limit of the material?
 - If limited: What is the effect of H₂ on the fatigue life of the material?
- How do S/N curves from tests in air (or inert fluid) and H₂ compare?

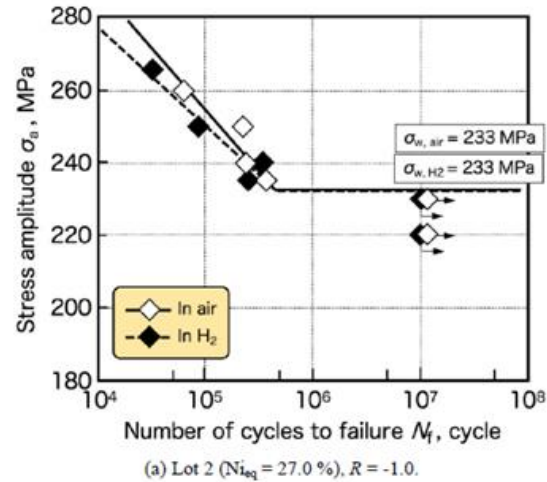


Fatigue testing

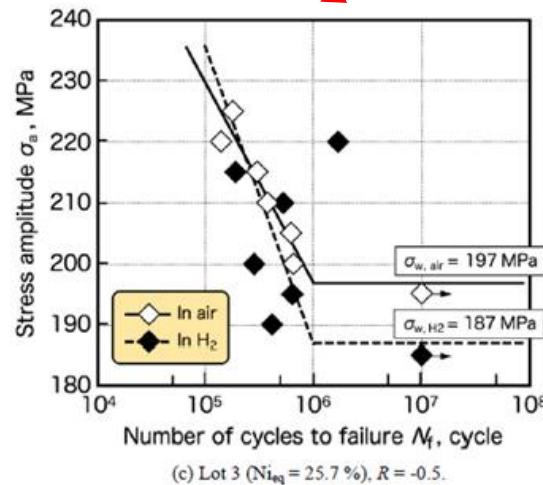
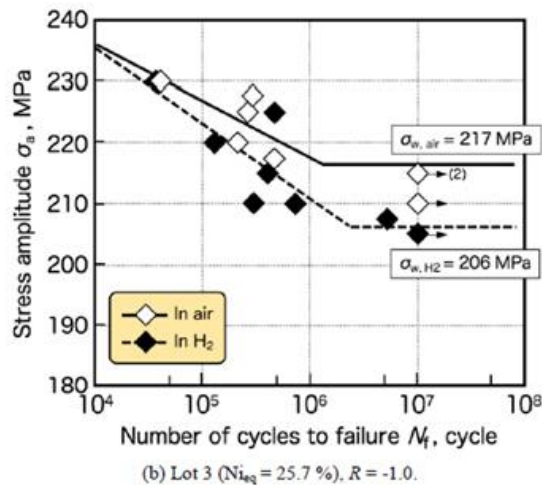


- Notched tensile sample
- $R = S_{\min} / S_{\max} = 0.1$
- Frequency 1Hz
- H_2 -charged or in H_2

Fatigue behavior

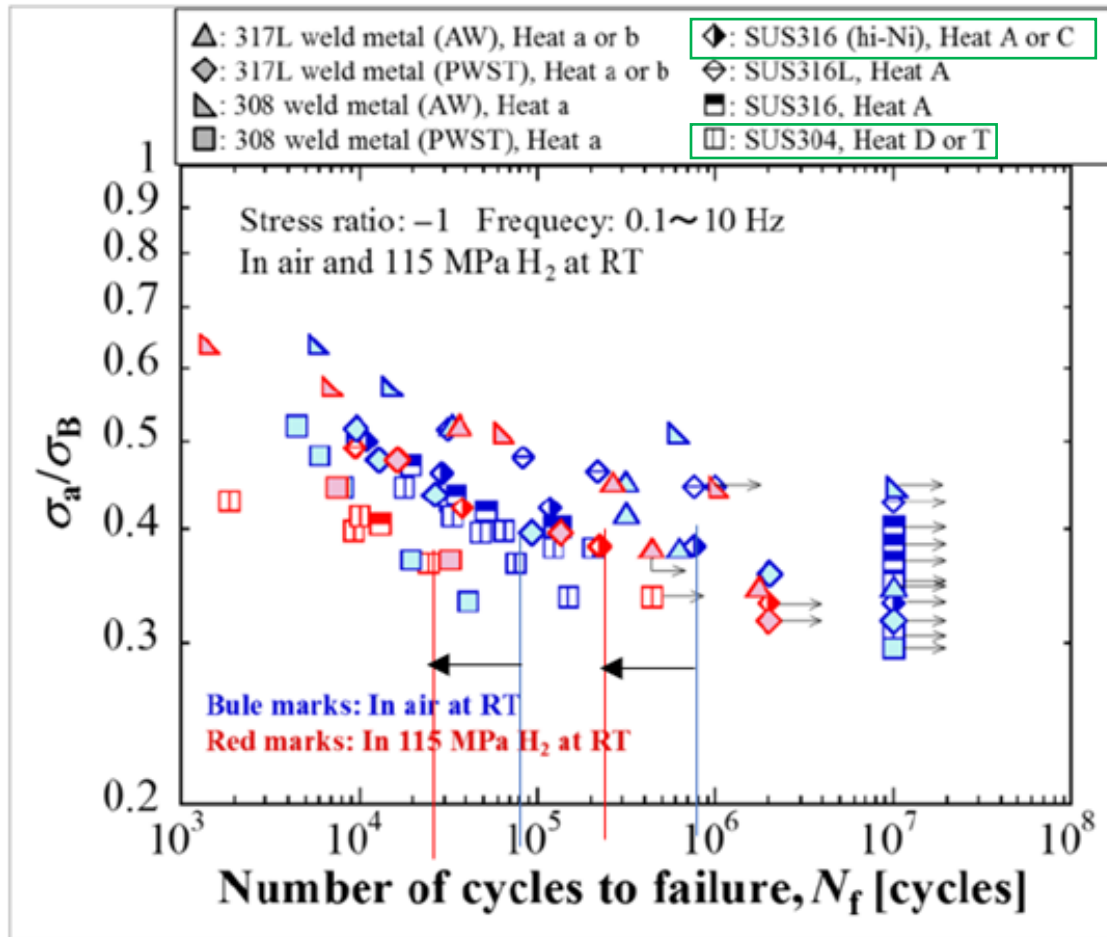


- H_2 reduced fatigue life
- For $Ni_{eq} = 27.0$, H_2 did not reduce fatigue limit
- For $Ni_{eq} = 25.7$, H_2 reduced fatigue limit by 5%



Akira Ueno, Guenec Benjamin, Effect of high-pressure H gas on tensile and fatigue properties of stainless steel SUS316L by means of the internal high-pressure H gas method, Procedia Structural Integrity 19 494–503 (2019)

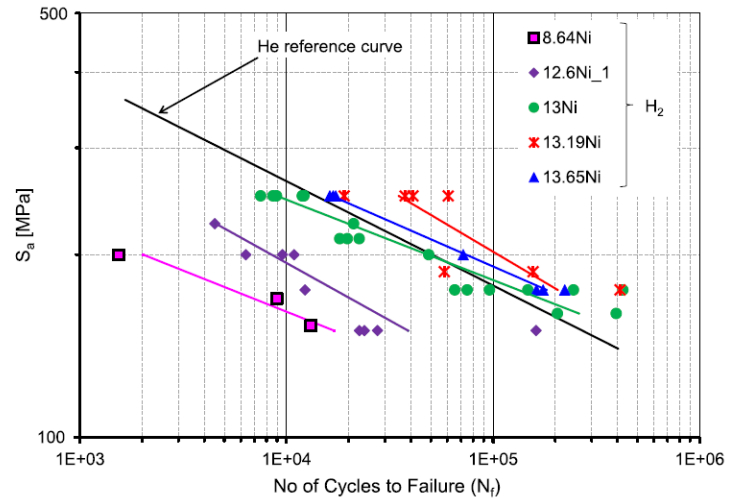
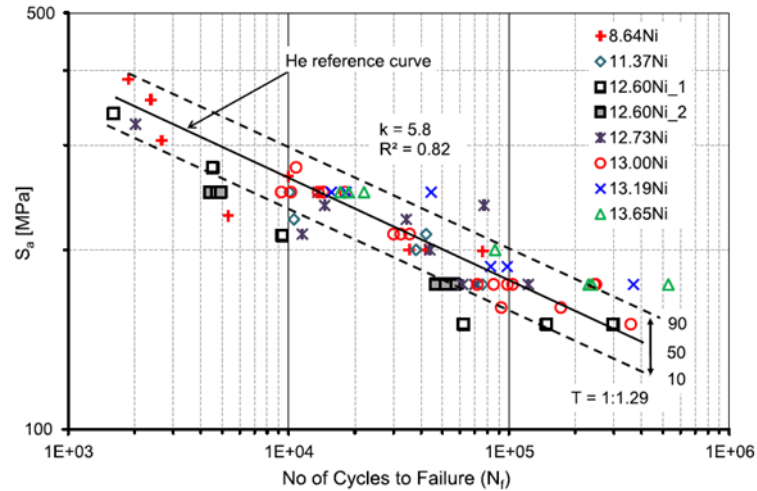
Fatigue behavior



- H_2 reduced fatigue life of 304 and 316L(hi-Ni) by about 70%
- The fatigue limit is about the same for 304 and 316L(hi-Ni)

M. Nakamura, S. Okazaki, H. Matsunaga, S. Matsuoka, Fatigue life properties of austenitic stainless steel welds in high-pressure hydrogen gas, in: JSME M&M 2017 Conference (Hokkaido, Japan, 2017)

Fatigue behavior

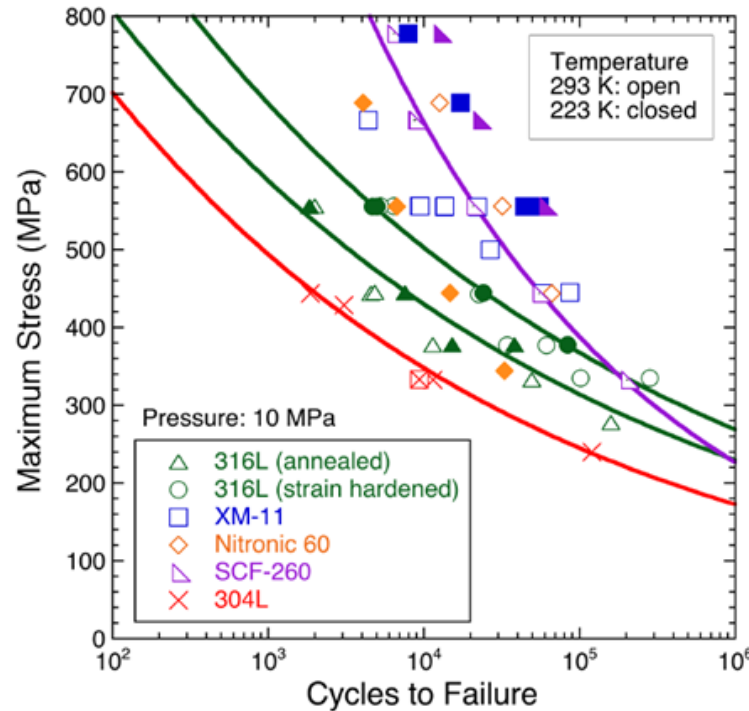
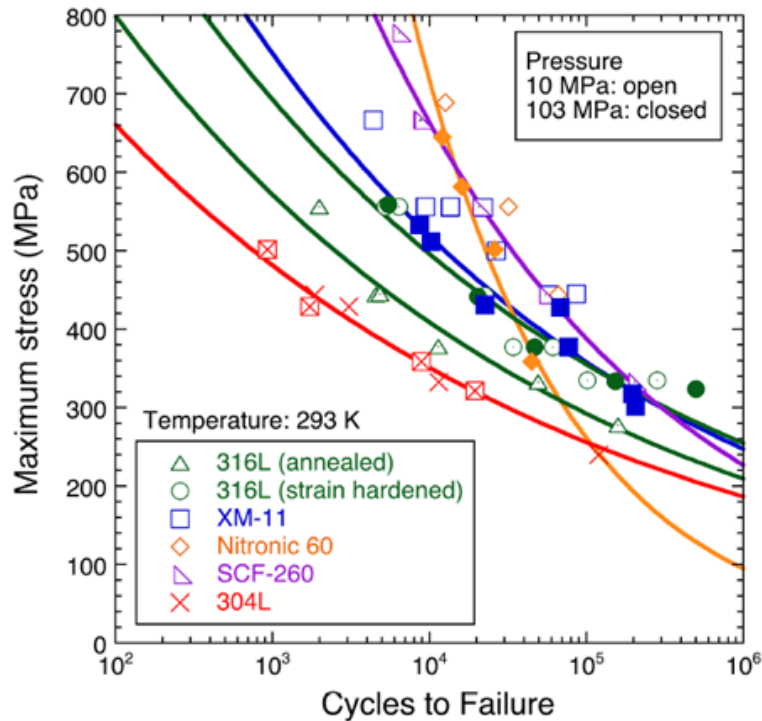


Thorsten Michler, Jörg Naumann, Jens Wiebesiek, Erich Sattler, Influence of frequency and wave form on S-N fatigue of commercial austenitic stainless steels with different nickel contents in inert gas and in high pressure gaseous hydrogen, International Journal of Fatigue 96 (2017) 67–77

Steel	Ni-eq	Nf(H2)/ Nf(He)	(Nf(He)-Nf(H2))/ Nf(He)
304	23 (?)	0.050	95%
12.6Ni (1)	28.2	0.340	66%
13.0Ni	29.1	1.000	0%
13.2Ni	28.2	1.000	0%
13.7Ni	31.8	0.700	30%

H₂ reduces fatigue life

Effect of H₂ pressure and temperature on fatigue life

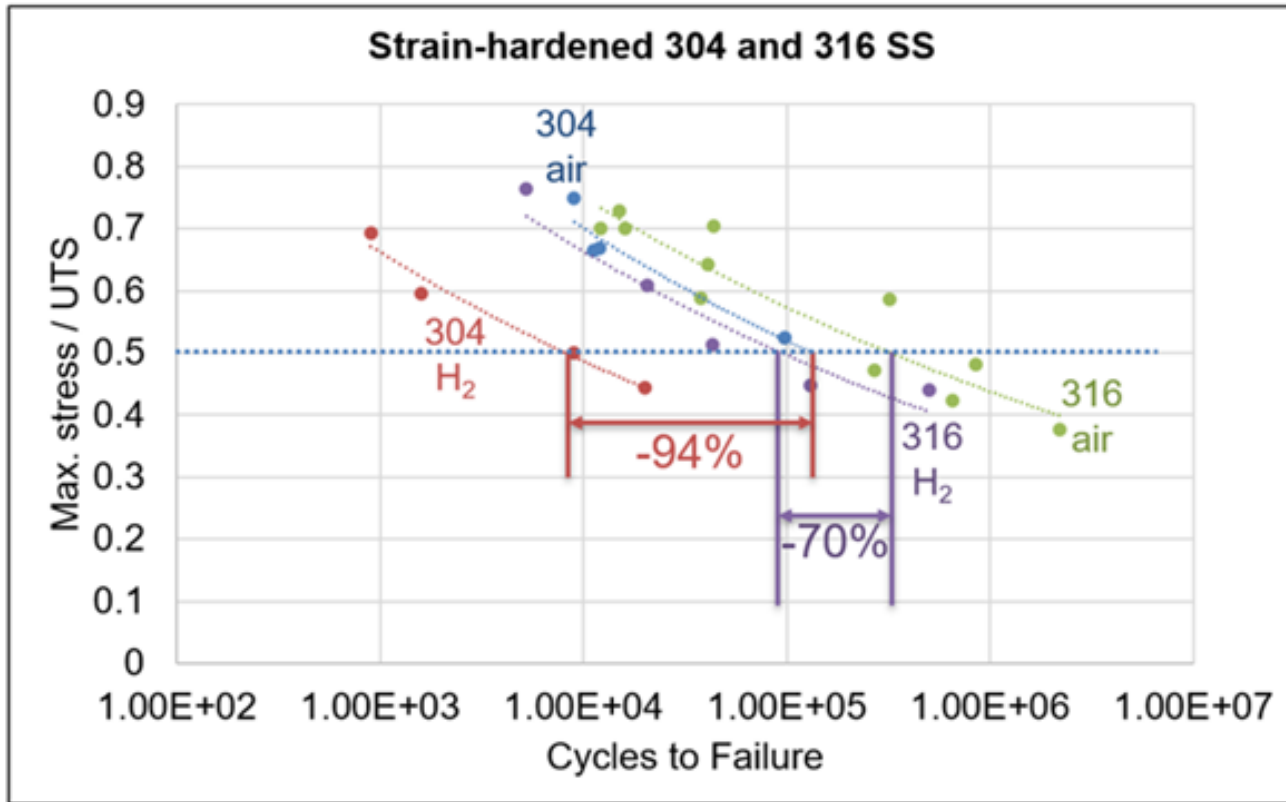


C. San Marchi, P. Gibbs, J. Foulk and K. Nibur, Fatigue life of austenitic stainless steels in hydrogen environments, in: 43rd MPA Seminar (Stuttgart, Germany, 2017)

Fatigue life of strain-hardened 316/316L:

- Comparable at 20°C in 10MPa (1.45ksi) and 103MPa (14.9ksi) H₂
- Comparable at -50°C and 20°C in 10MPa (1.45ksi) H₂

Loss in fatigue life



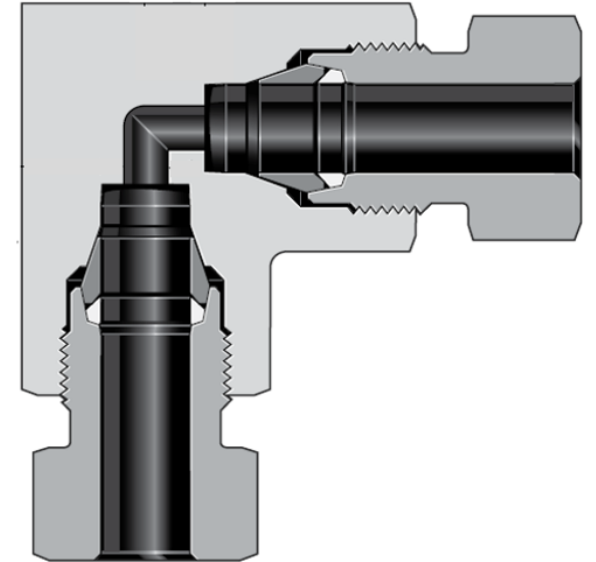
Alloy	Ni-eq	Loss
304	22.3	-94%
316	27.1	-70%



- Testing performed at RT in air and in H₂ (103MPa)

Hydraulic pressure cycling of 6mm & 1/2" FK elbows

- Qualification of FK fittings per EC79
 - Tested 3 fittings each, 6mm (6MFK) and 1/2" (8FK)
 - 150,000 cycles, 0.1Hz
 - Between 20 bar (0.29 ksi) & 875 bar (12.7 ksi)
 - No failures observed



Summary – Effect of H₂ on 316 SS

- Increases yield and tensile strength
- Reduces ductility (mainly RA), especially if:
 - Ni-content < 12%
 - Temperature between 0°C and -100°C
- Reduces fatigue life
 - Less reduction with increasing Ni-content
 - H₂ accelerates rate of crack propagation
- Does not reduce fatigue limit
 - Possibly small reduction if Ni-content <12%

Summary – Effect of H₂ on 316 SS (cont.)

- Hydrogen itself does not cause fatigue cracking
- High-pressure cycling can cause fatigue cracking
 - High pressure amplitudes
 - Crack initiation at locations of high stress concentration
 - Bore intersections
 - Material surface defects



