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Hydrogen Effects in Type 316 Stainless Steel and SAF 2507 Super Duplex Stainless Steel

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Motivation

- Stainless steels will likely find application for high-pressure, small-diameter piping and components in the nascent infrastructure of the proposed hydrogen-based economy. Type 316 stainless steel is particularly attractive for high-pressure gaseous hydrogen service because:
  - it benefits from a broad experience-base in hydrogen-producing aqueous environments
  - it is resistant to deformation-induced microstructural changes (i.e., martensite transformation)
  - a few key studies have shown it to be more resistant to fracture in high-pressure hydrogen gas compared to other common stainless steels.
- In this study, we explore *hydrogen-assisted fracture* in several 316 alloys and a high-strength alternative to 316, super duplex stainless steel SAF 2507.
- Several materials variables are compared:
  - <u>Strength</u>: annealed compared to cold-worked microstructures
  - <u>Composition</u> of 316 alloys:
    - Nickel content ranging from 11 to 13.5 wt%
    - Carbon content: 316 and 316L alloys
  - <u>Microstructure</u>: stable austenitic stainless steel (316) compared to duplex (austenite-ferrite) stainless steel

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Methodology

- Two types of mechanical tests were employed to study *hydrogen-assisted fracture*:
  - Smooth Bar Tensile Testing
  - J-integral Fracture Toughness Testing using Single-Edge Bend (SEB) specimens (only cold-worked materials were testedin the LR orientation)
- All testing was performed in laboratory air
- Triplicate specimens were tested for most conditions, although in some cases only two specimens were tested; all reported values are averages of all tests
- Specimens were tested in two conditions:
  - As-machined (uncharged) condition
  - With internal hydrogen thermally precharged from the gas phase
    - 138 MPa hydrogen gas at 573 K for 10 to 30 days depending on geometry to produce uniform hydrogen concentration through the cross-section of the specimens
    - Resulting hydrogen contents (averages of several measurements):
      - 316 alloys: 136 wppm hydrogen (0.76 wt%)
      - SAF 2507: 125 wppm hydrogen (0.70 wt%)

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Methodology

- Thermal precharging supersaturates the materials with hydrogen relative to room temperature
  - This represents an exaggerated hydrogen concentration after exposure to gaseous hydrogen environments
  - Internal hydrogen, however, does not replicate the conditions at a crack tip where external hydrogen is a source for hydrogen uptake to the hydrostatic stress field at the tip of a crack

$$c_s = c_H \exp\left({V_H \bar{\sigma}} / {RT} \right)$$

where c_s is the hydrogen concentration in the stressed lattice, V_H is the partial molar volume of hydrogen in the steel lattice (~2 cm^3 mol^{-1}) and $\bar{\sigma}$ is the hydrostatic stress (near the crack tip)

  - The hydrogen concentration achieved at equilibrium at 573 K is estimated to be of similar magnitude in austenitic stainless steels to the enhanced concentration due to the hydrostatic stress state at a crack tip at room temperature

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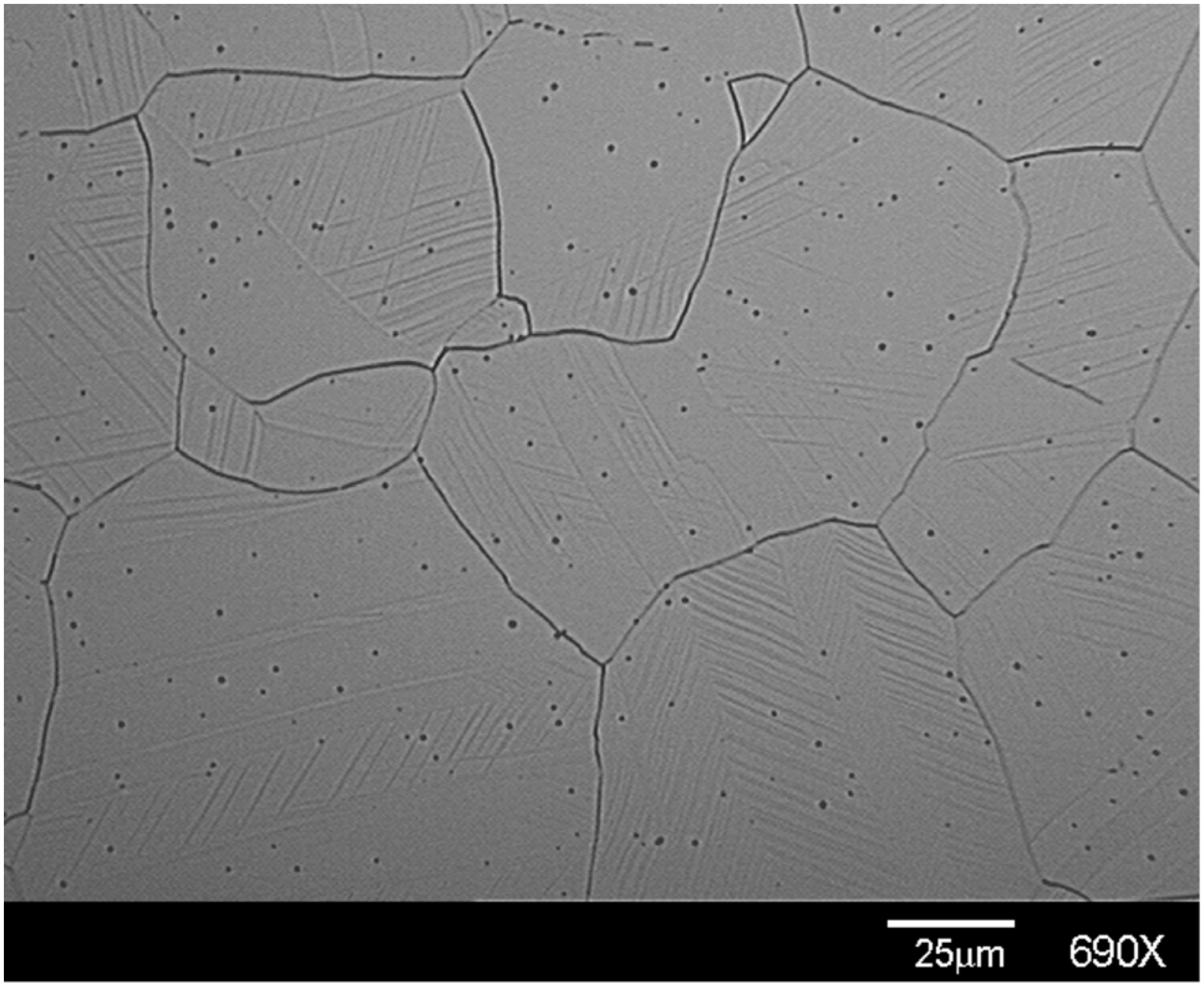
Materials

Four materials were tested

- High-strength corrosion-resistant substitute for 300-series stainless steel: super duplex stainless steel, alloy SAF 2507
  - This alloy is composed of approximately 50% ferrite and 50% austenite
- Three 316 stainless steels:
  - Premium grade: 316L VIM/VAR with high Ni and low inclusion content
  - Standard grade: 316 with high carbon and moderate Ni
  - Off-the-shelf: 316L with relatively low alloy content

	Fe	Cr	Ni	Mn	Mo	N	C	Si	S	P
Super Duplex Stainless Steel, SAF 2507 (UNS32750)	Bal	25.22	6.94	0.46	3.9	0.287	0.011	0.25	0.0006	0.019
316	Bal	17.72	12.13	1.69	2.36	0.03	0.041	0.57	0.027	0.026
316L VIM/VAR	Bal	17.7	13.5	0.31	2.63	0.01	0.017	0.35	0.006	0.011
316L	Bal	16.63	11.07	1.29	2.02	0.023	0.03	0.49	0.024	0.03

Materials



316L VIM/VAR
Cold-Worked Bar

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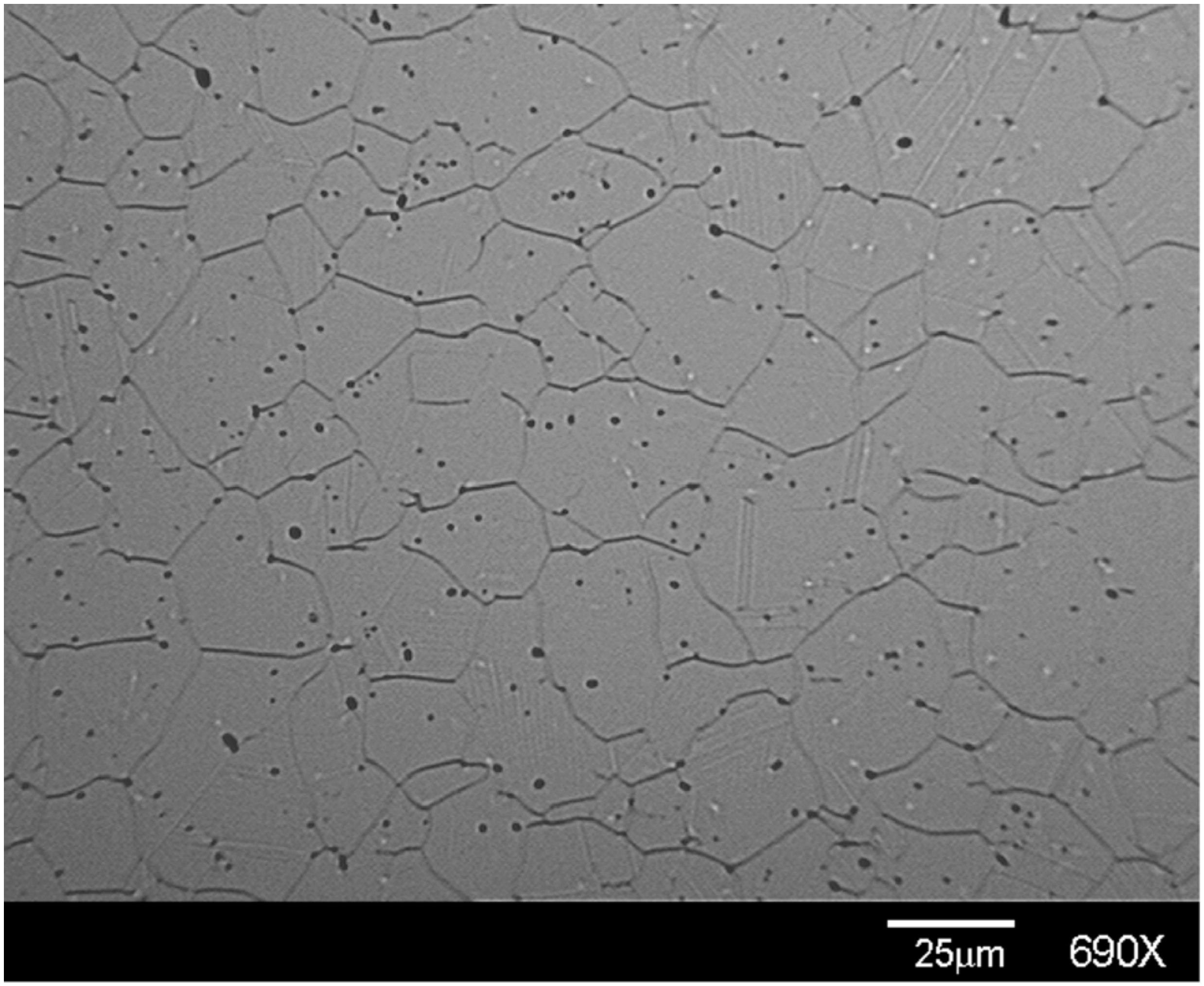
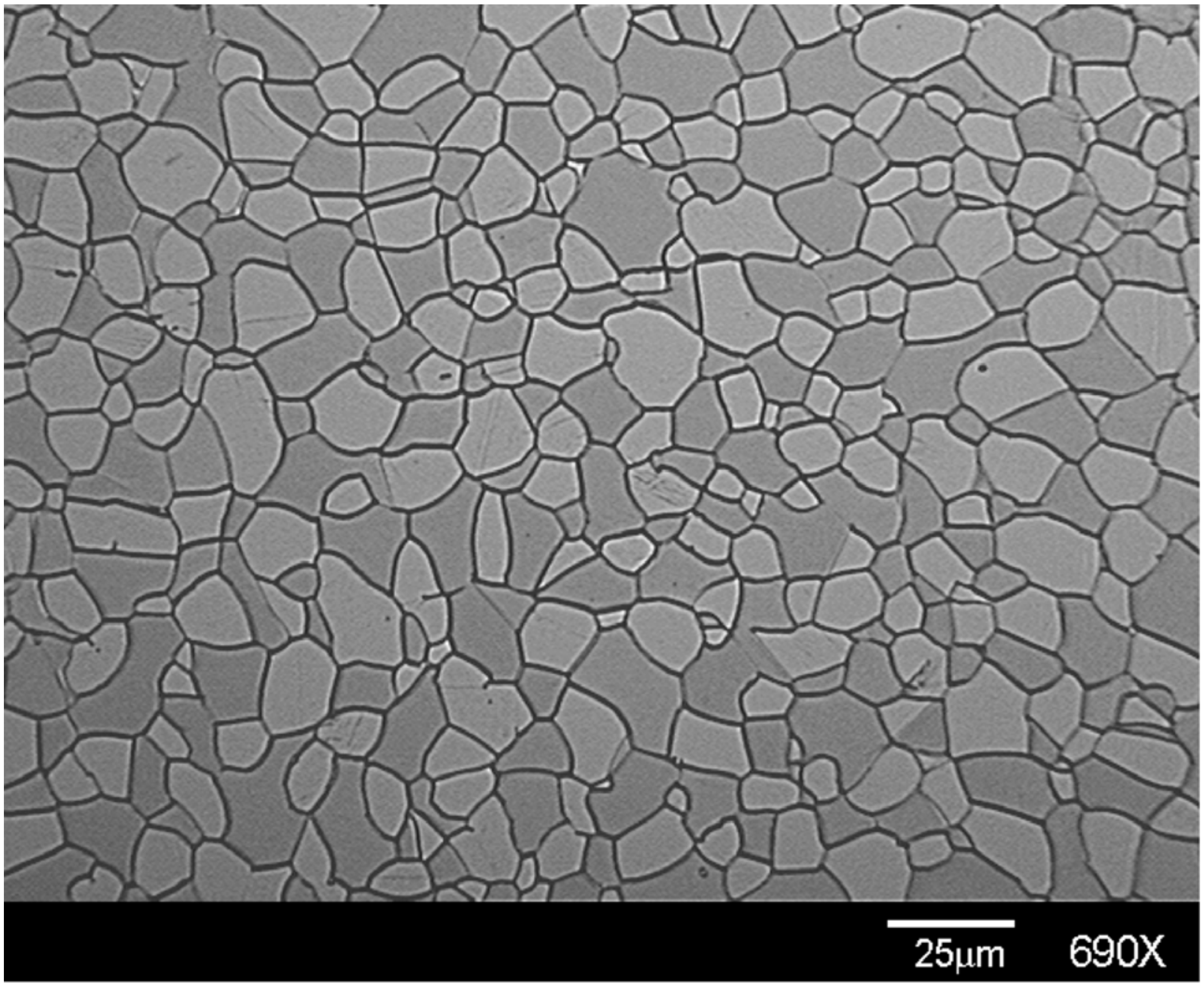
Materials



316L
Cold-Worked Bar

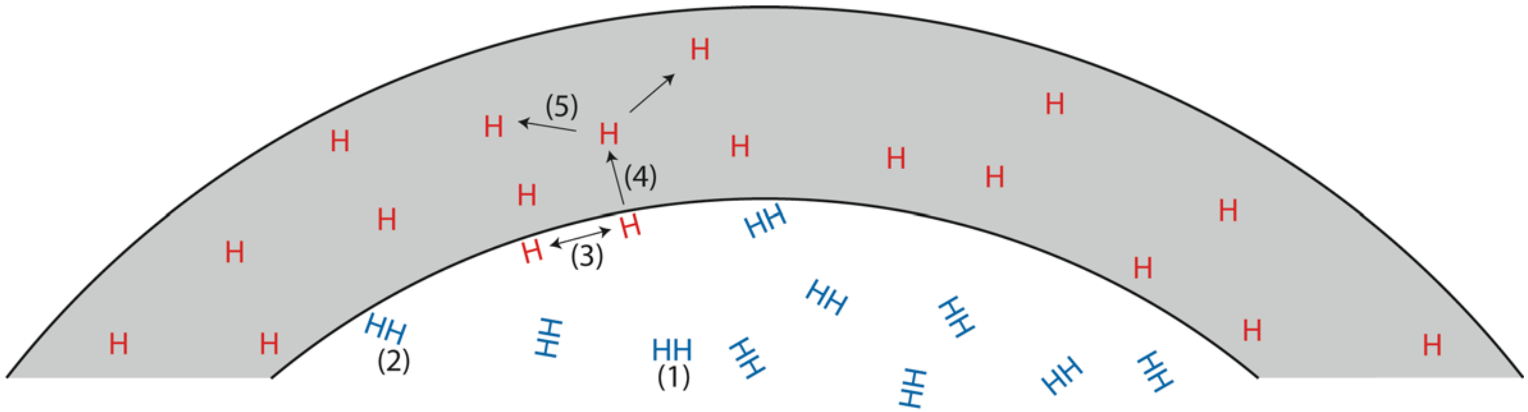
Materials



SAF2507
Cold-Worked Bar

Hydrogen Assisted Fracture in Metals

Hydrogen dissolves into metals where it interacts with the microstructure to assist deformation and fracture by a number of processes generally referred to as hydrogen embrittlement



Chemical Equilibrium: $\frac{1}{2}H_2 \leftrightarrow \underline{H}$

(1) Hydrogen gas
(2) Physisorption
(3) Dissociation
(4) Dissolution
(5) Diffusion

Solubility $c_H = Kf^{1/2}$

Diffusivity $J_\infty = D\frac{c_H}{t} = \frac{DK}{t} f^{1/2}$

Permeability $\phi \equiv DK$

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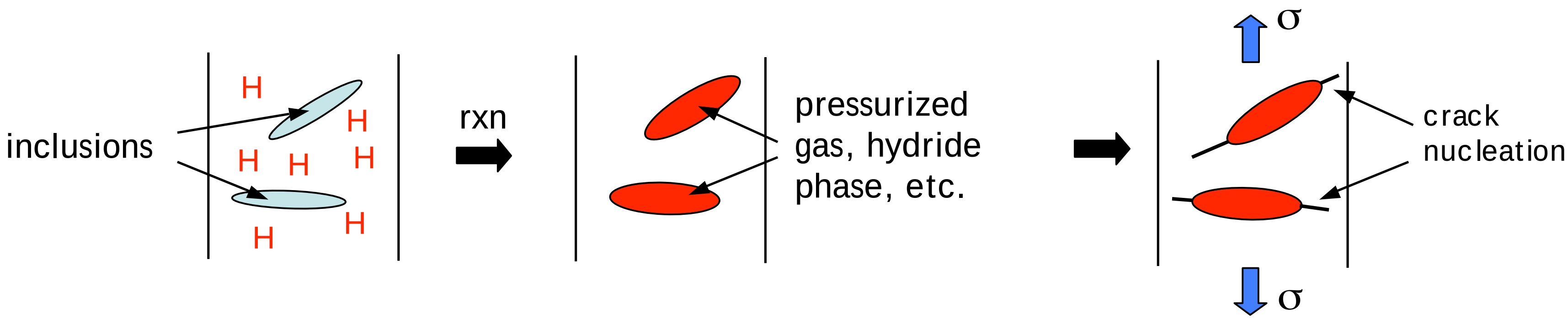
Hydrogen-Assisted Fracture Mechanisms in Metals

Hydrogen attack

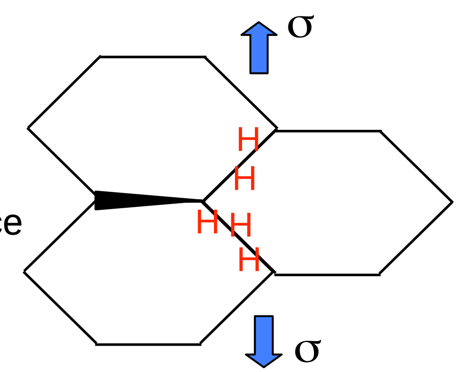
- chemical reaction of atomic hydrogen with microstructural features

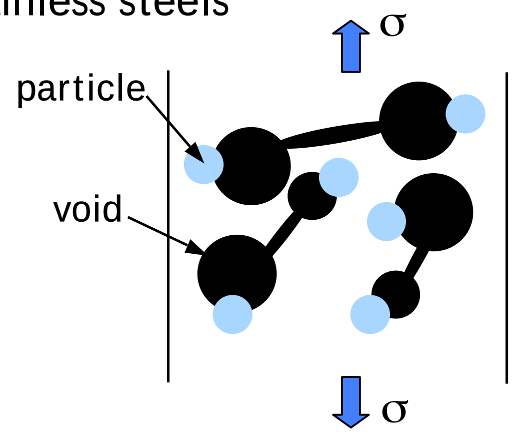


Hydrogen solute effects

- solute hydrogen enhanced failure of interfaces and deformation mechanisms
- class of mechanisms affecting stainless steels

Hydrogen accumulation at interfaces affects strength of interface (grain boundaries, second phases, inclusions)





Hydrogen enhanced shear localization

Hydrogen Solubility

- Thermodynamic equilibrium of hydrogen dissolution in a metal

$$\tfrac{1}{2}\mathrm{H}_2 \leftrightarrow \underline{\mathrm{H}}$$

- Hydrogen content is determined from thermodynamic equilibrium:

$$c_H = Kf^{1/2}$$

where c_H is the equilibrium concentration of hydrogen dissolved in a metal, K is the equilibrium constant and f is the fugacity of the hydrogen

Hydrogen Solubility

- Equilibrium constant for 300-series stainless steel

$$K = 135 \exp(-710/T)$$

- Fugacity of hydrogen gas is function of temperature (T) and pressure (P):

Abel-Noble equation of state

$$f = P \exp(Pb/RT)$$

where R is the universal gas constant (8.31447 J mol^{-1} K^{-1}) and for hydrogen b = 15.84 cm^3 mol^{-1}.

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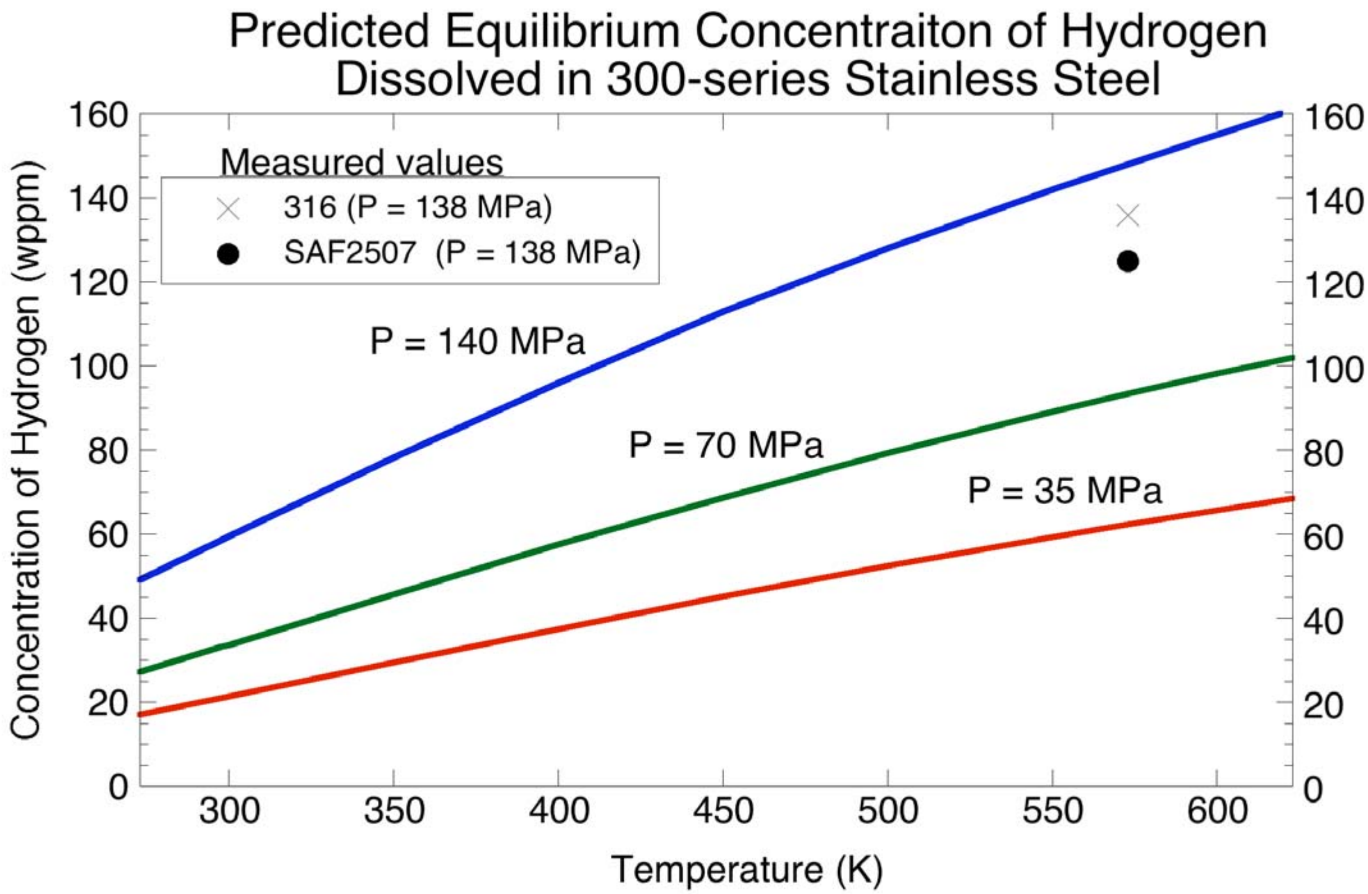
Hydrogen Solubility



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Results

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Tensile properties

Material	Condition	Yield Strength S_y (MPa)	Tensile Strength S_u (MPa)	Reduction of Area RA (%)	Uniform Elongation El_u (%)	Total Elongation El_t (%)
SAF 2507 Annealed bar	uncharged	647	879	85	25	48
	precharged	745	914	46	24	35
SAF 2507 Cold-worked bar	uncharged	988	1110	80	1.2	26
	precharged	1208	1221	25	1.0	12
316 Annealed bar	uncharged	257	602	80	54	67
	precharged	311	651	69	55	66
316 Cold-worked bar	uncharged	563	735	78	26	47
	precharged	665	811	66	25	45
316L VIM/VAR Annealed bar	uncharged	221	551	85	57	71
	precharged	279	607	72	60	71
316L VIM/VAR Cold-worked bar	uncharged	594	736	78	20	41
	precharged	690	812	68	21	40
316L Annealed bar	uncharged	253	585	81	58	70
	precharged	306	642	62	57	66
316L Cold-worked bar	uncharged	583	722	78	24	45
	precharged	694	819	59	23	41

Hydrogen precharging: 138 MPa hydrogen gas, 573 K, 10 days.

SAF 2507: 125 wppm hydrogen (0.70 at%)

316 alloys: 136 wppm hydrogen (0.76 at%)

All testing was performed at room temperature in air with a constant displacement rate of 0.02 mm s^{-1} corresponding to a strain rate in the plastic regime of ~1.2×10^{-3} s^{-1}.

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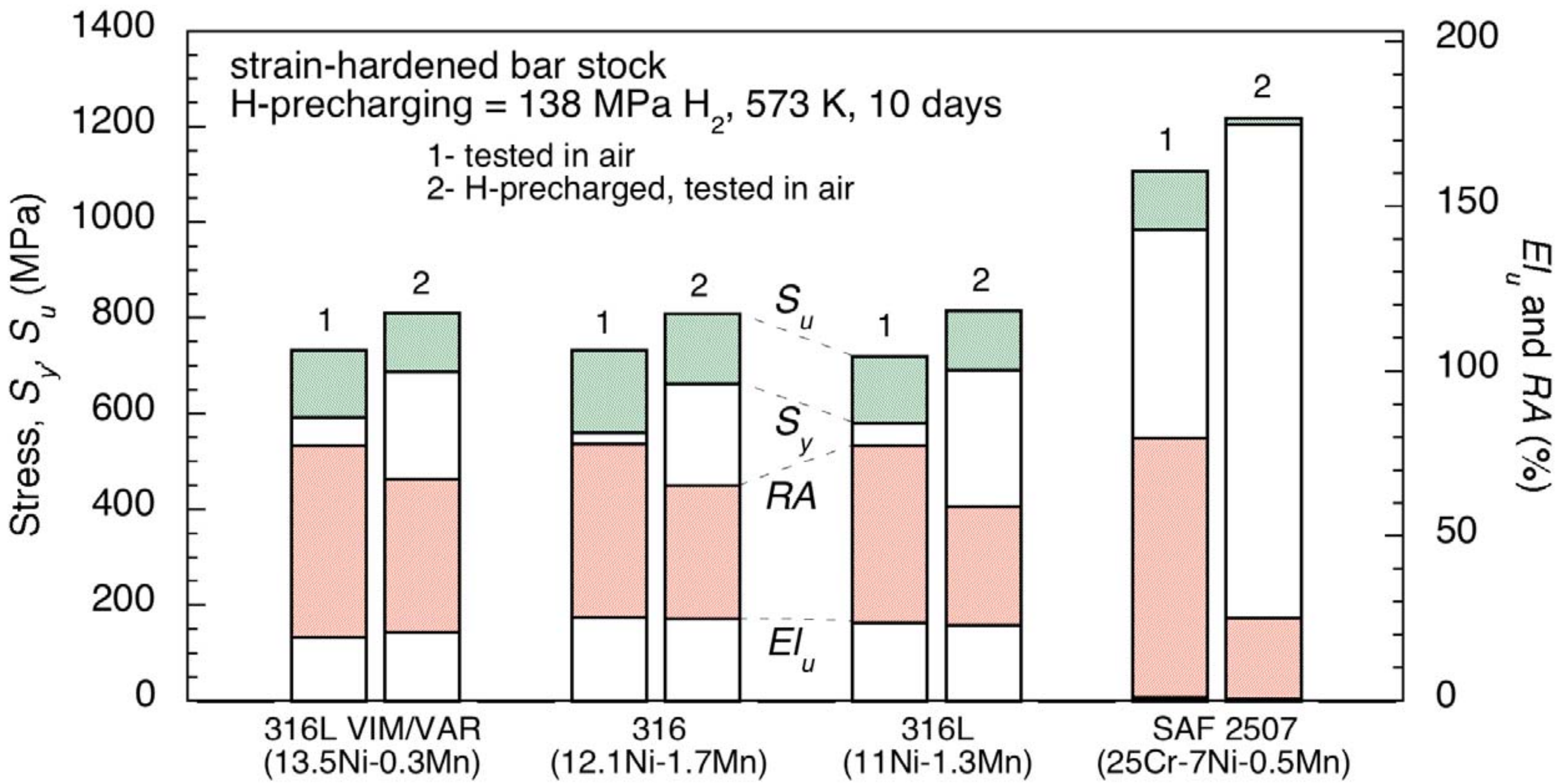
Tensile properties

For austenitic stainless steels:

- Strength properties are generally enhanced
- Ductility is characterized by clear difference in reduction of area (RA)



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Tensile properties

The relative properties provide a gauge for comparing property changes under specific environmental conditions: values >1 indicate an improvement in properties as observed for strength; values <1 indicate a degradation in property as observed for ductility (RA and elongations)

Material	RS_y	RS_u	RRA	REl_u	REl_t
SAF 2507 Annealed bar	1.15	1.05	0.54	0.95	0.73
SAF 2507 Cold-worked bar	1.22	1.10	0.32	0.79	0.48
316 Annealed bar	1.21	1.08	0.87	1.02	0.99
316 Cold-worked bar	1.18	1.10	0.84	0.98	0.95
316L VIM/VAR Annealed bar	1.26	1.10	0.84	1.05	1.00
316L VIM/VAR Cold-worked bar	1.16	1.10	0.87	1.07	0.96
316L Annealed bar	1.21	1.10	0.76	0.99	0.94
316L Cold-worked bar	1.19	1.13	0.76	0.98	0.92

$$RS_y = \frac{S_y(\text{H precharged})}{S_y(\text{uncharged})} \qquad RRA = \frac{RA(\text{H precharged})}{RA(\text{uncharged})} \qquad REl_t = \frac{El_t(\text{H precharged})}{El_t(\text{uncharged})}$$

$$RS_u = \frac{S_u(\text{H precharged})}{S_u(\text{uncharged})} \qquad REl_u = \frac{El_u(\text{H precharged})}{El_u(\text{uncharged})}$$

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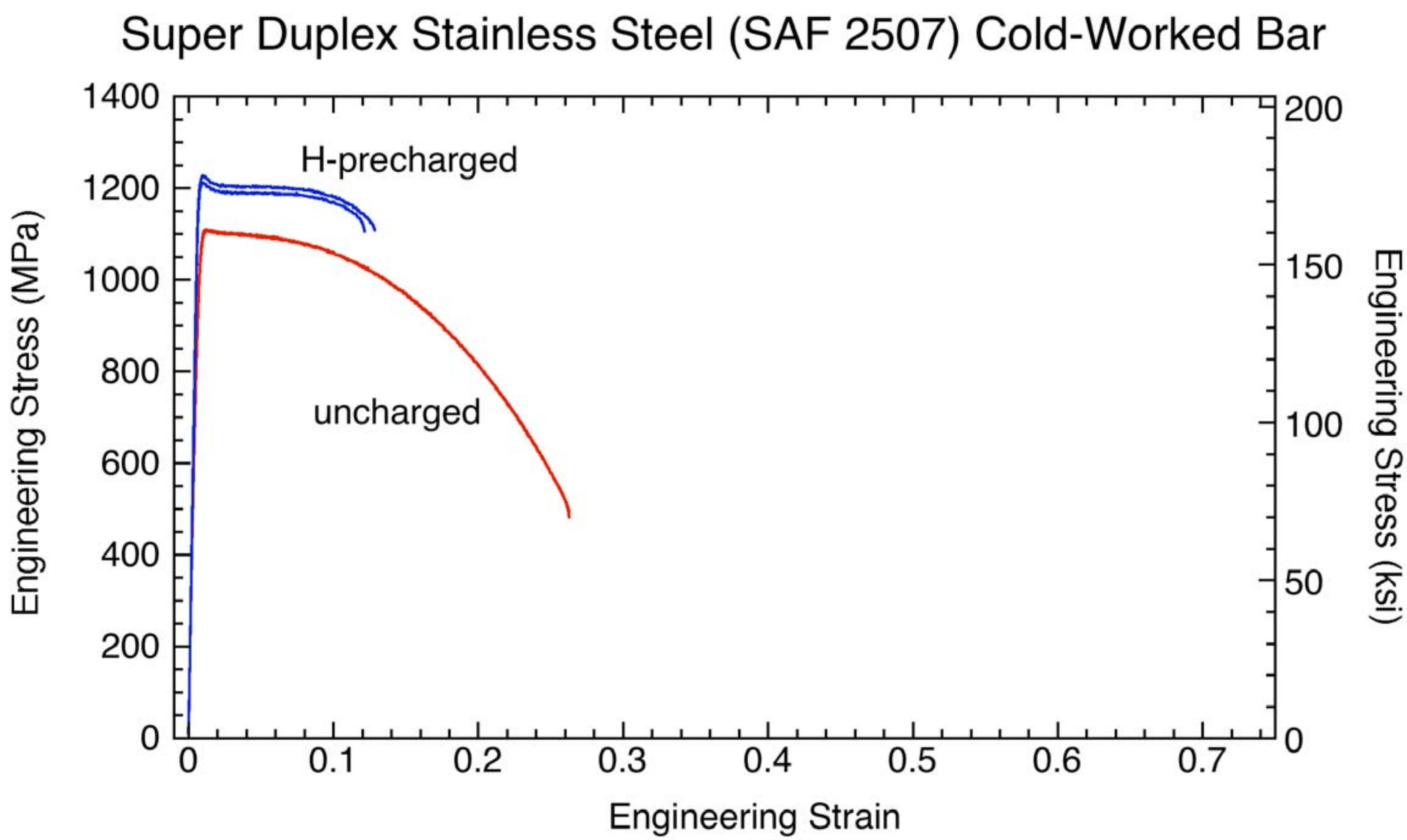
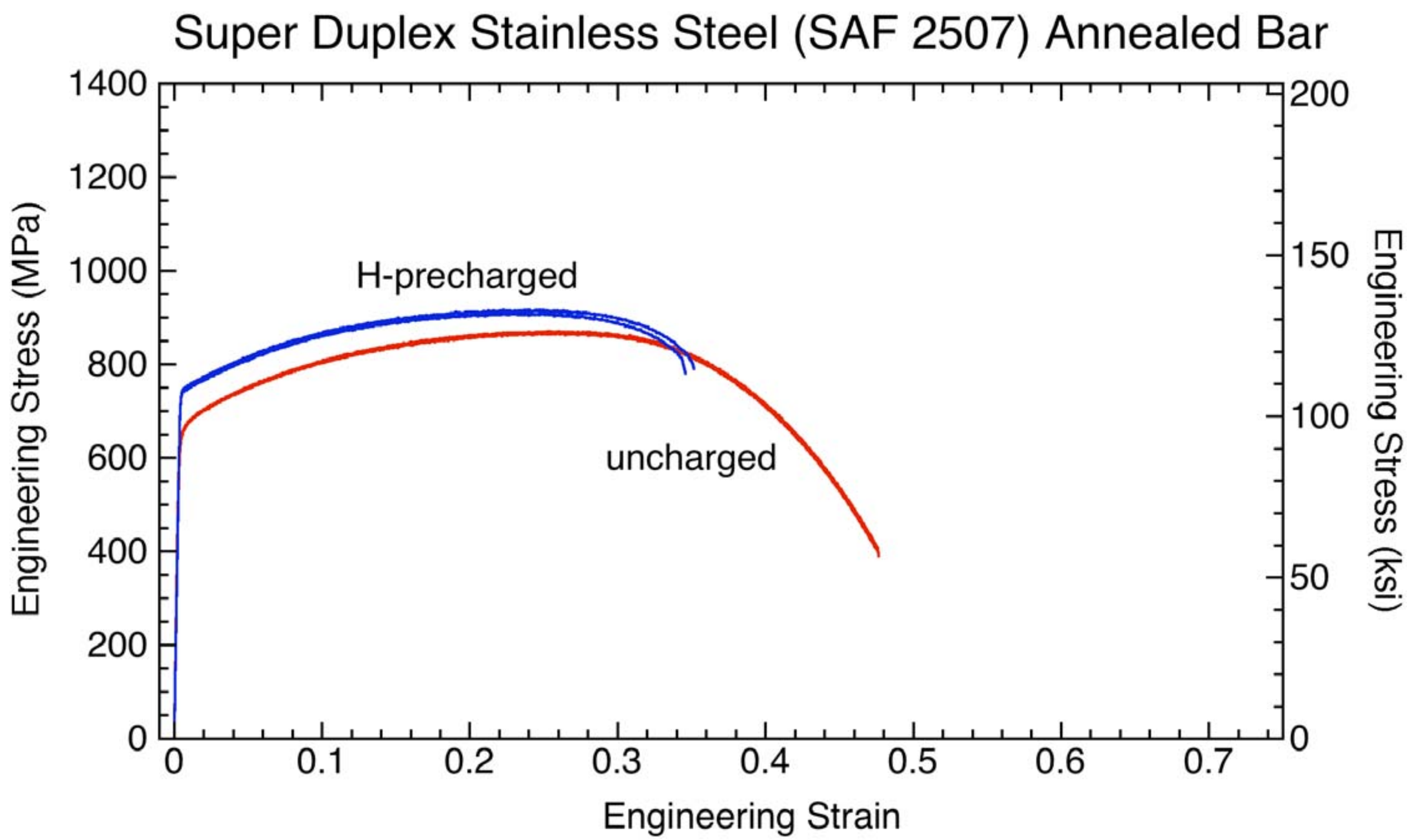
Tensile Flow Curves

SAF 2507 Cold-Worked Bar



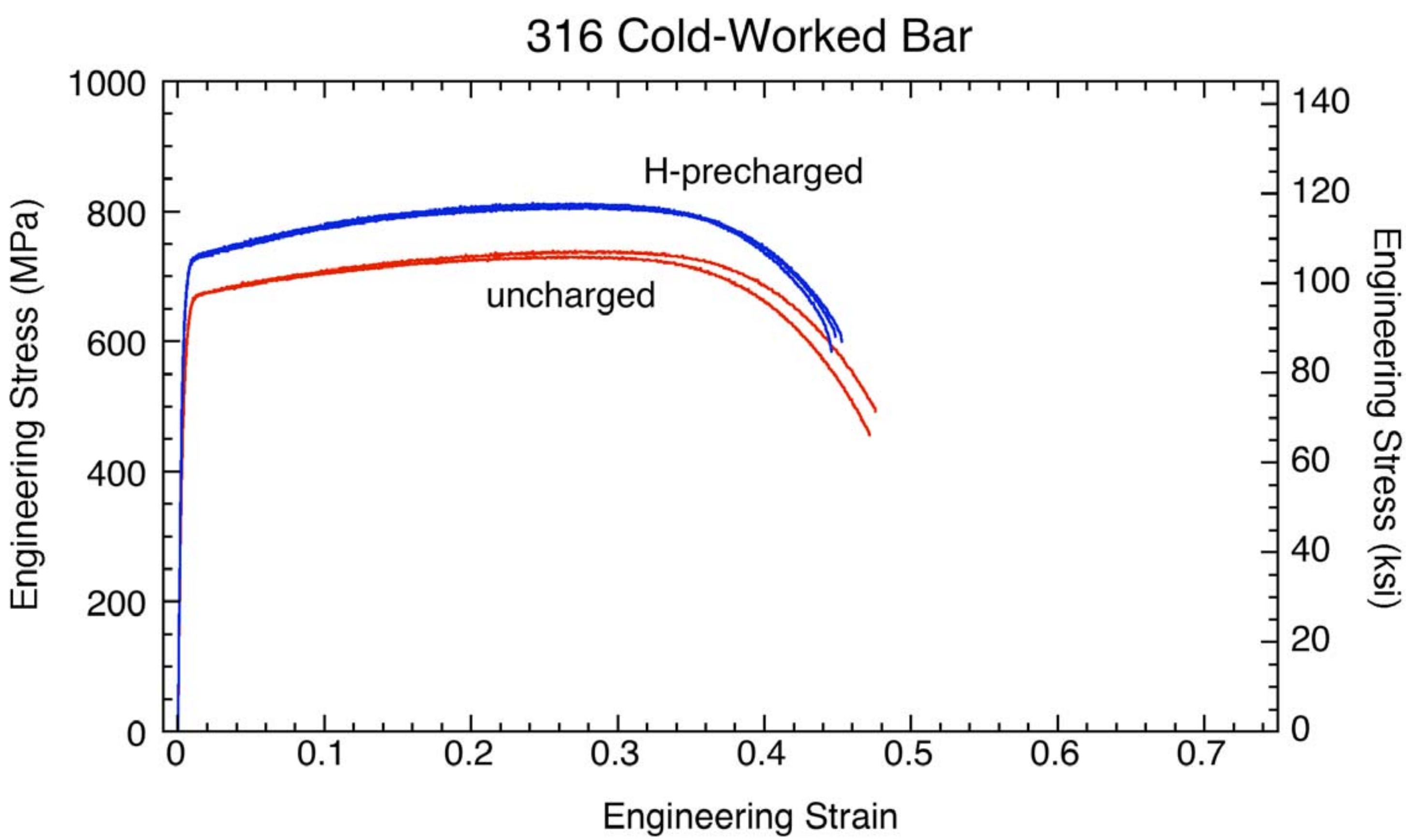
Tensile Flow Curves

SAF 2507 Annealed Bar



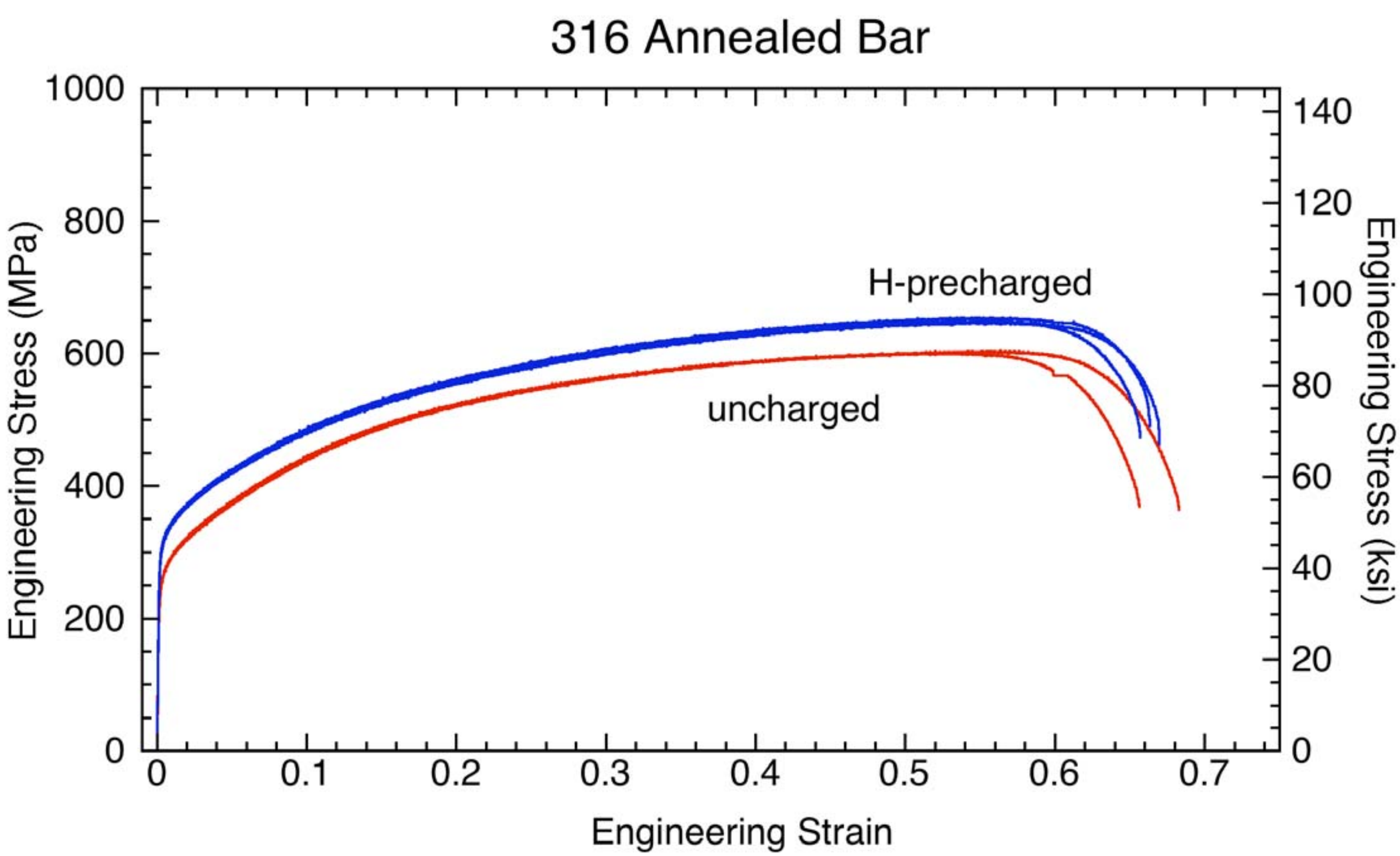
Tensile Flow Curves

316 Cold-Worked Bar



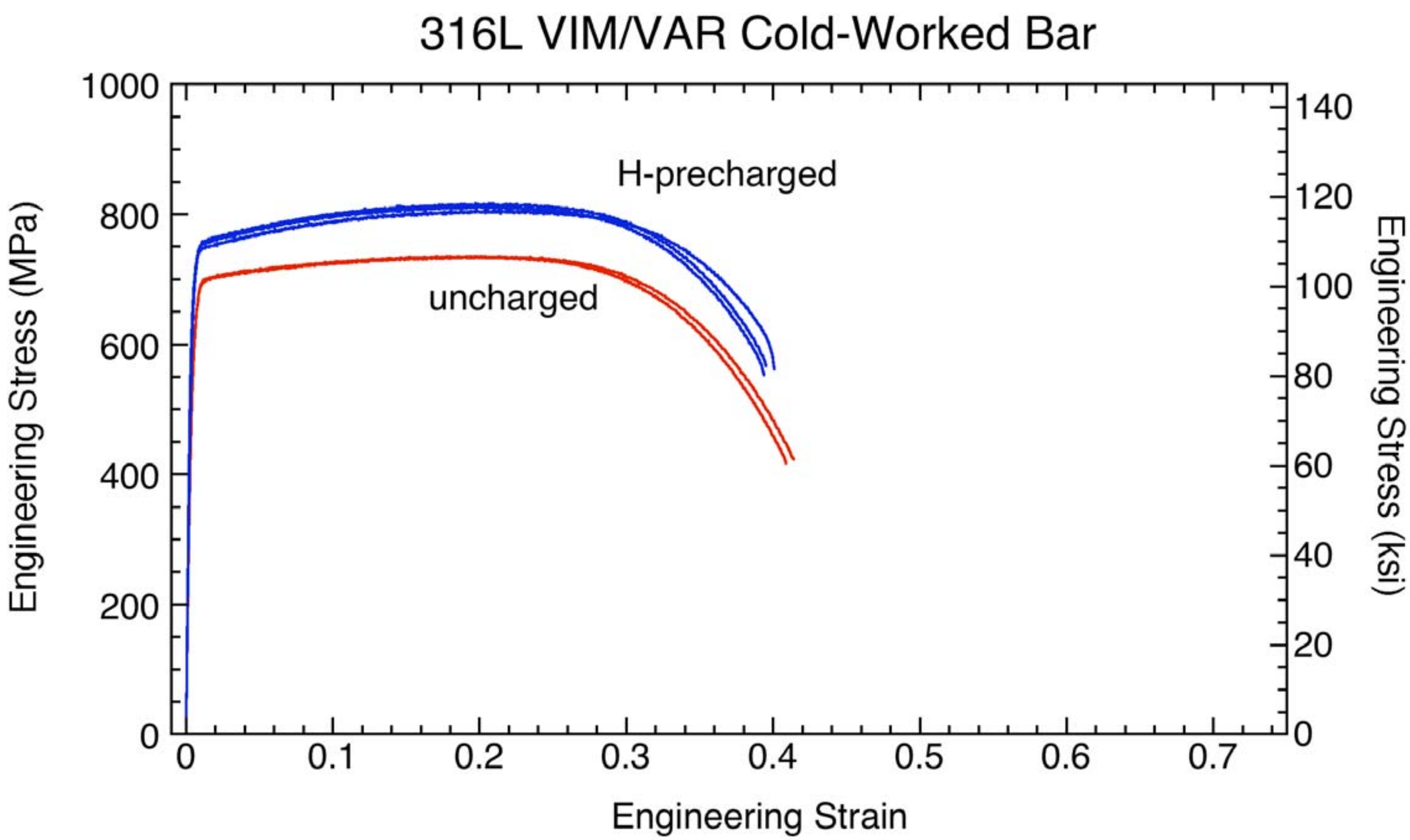
Tensile Flow Curves

316 Annealed Bar



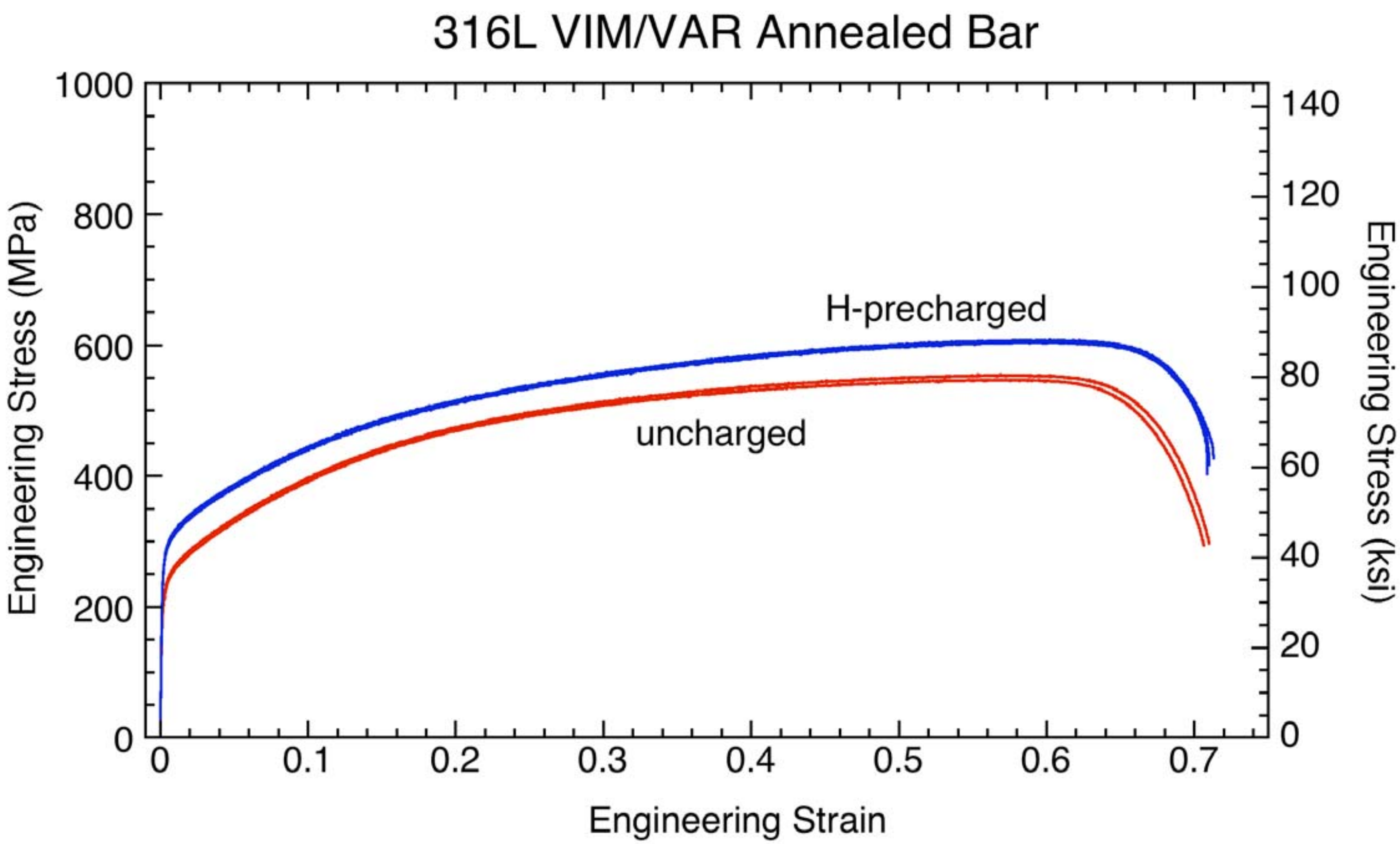
Tensile Flow Curves

316L VIM/VAR Cold-Worked Bar



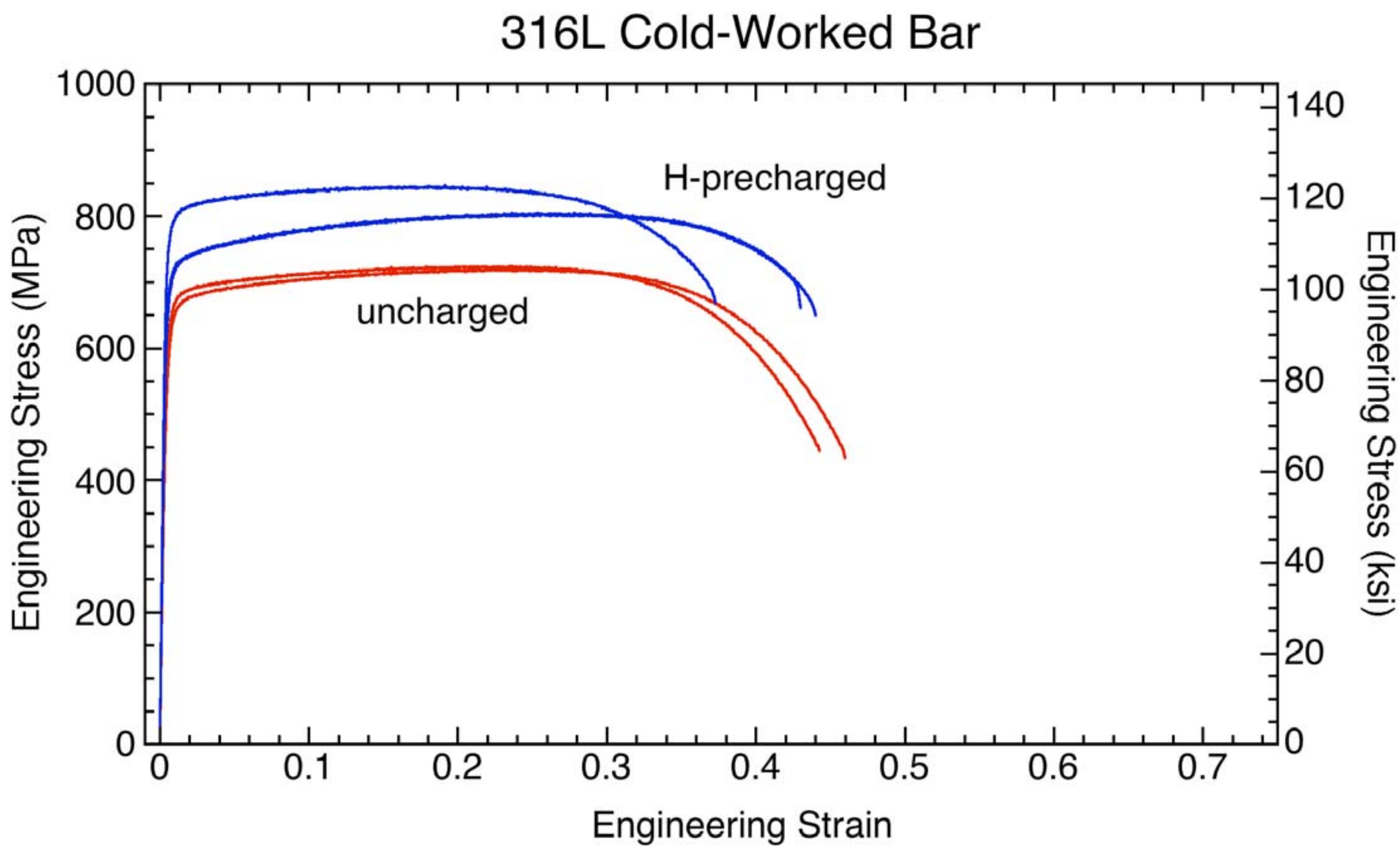
Tensile Flow Curves

316L VIM/VAR Annealed Bar



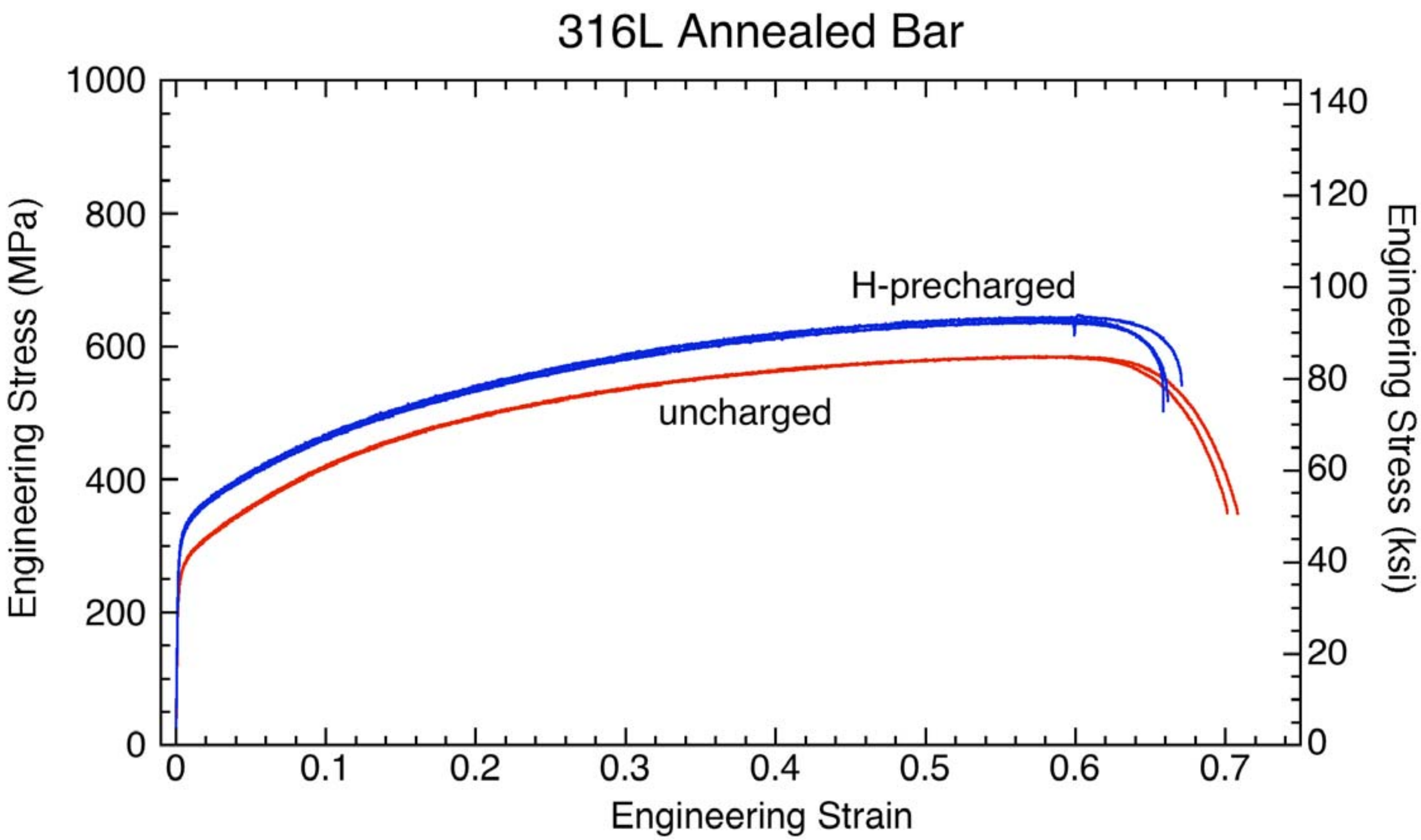
Tensile Flow Curves

316L Cold-Worked Bar



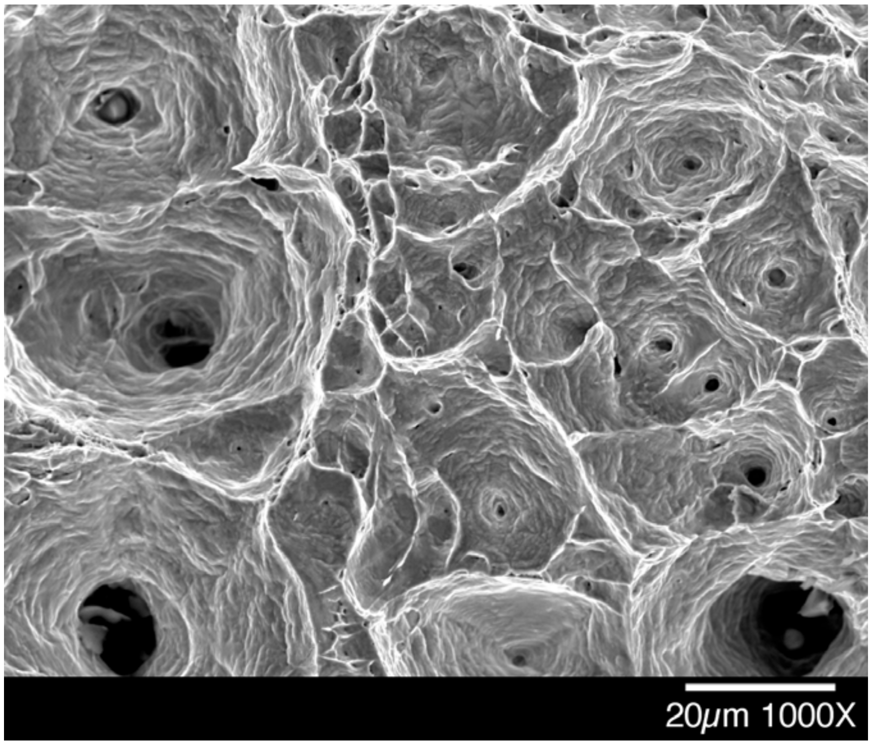
Tensile Flow Curves

316L Annealed Bar



Fracture Surfaces: Tensile

SAF 2507, Cold-Worked Bar



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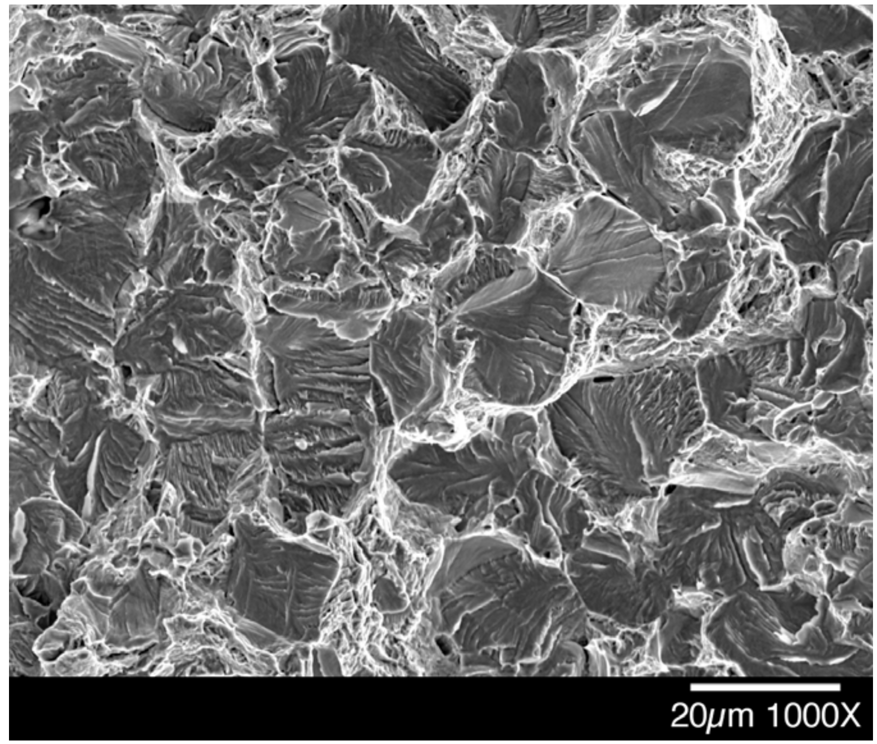
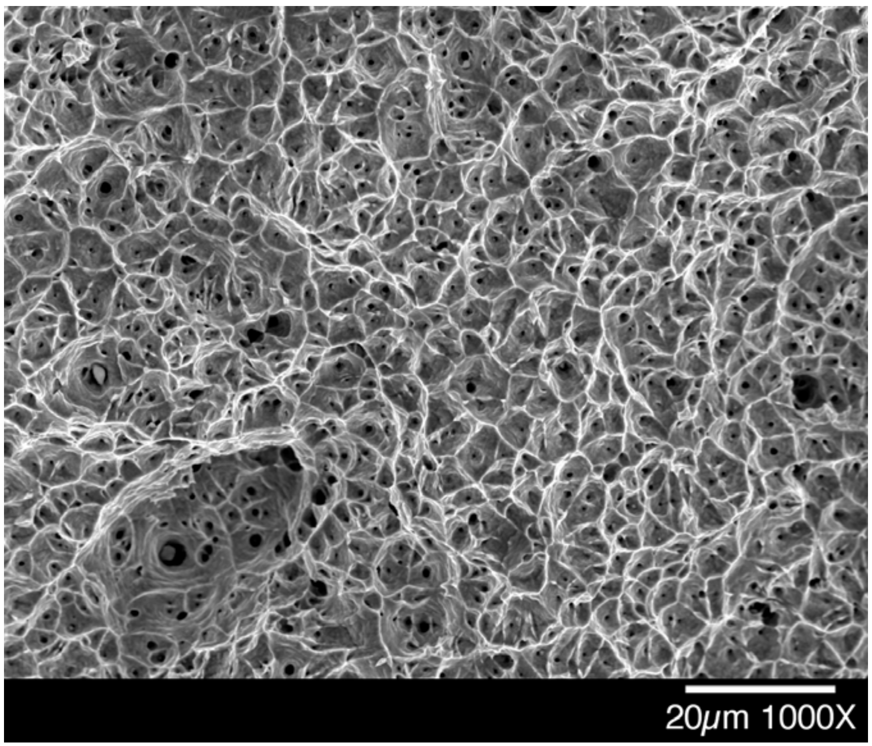


Thermally precharged

Fracture Surfaces: Tensile

316L VIM/VAR, Cold-Worked Bar



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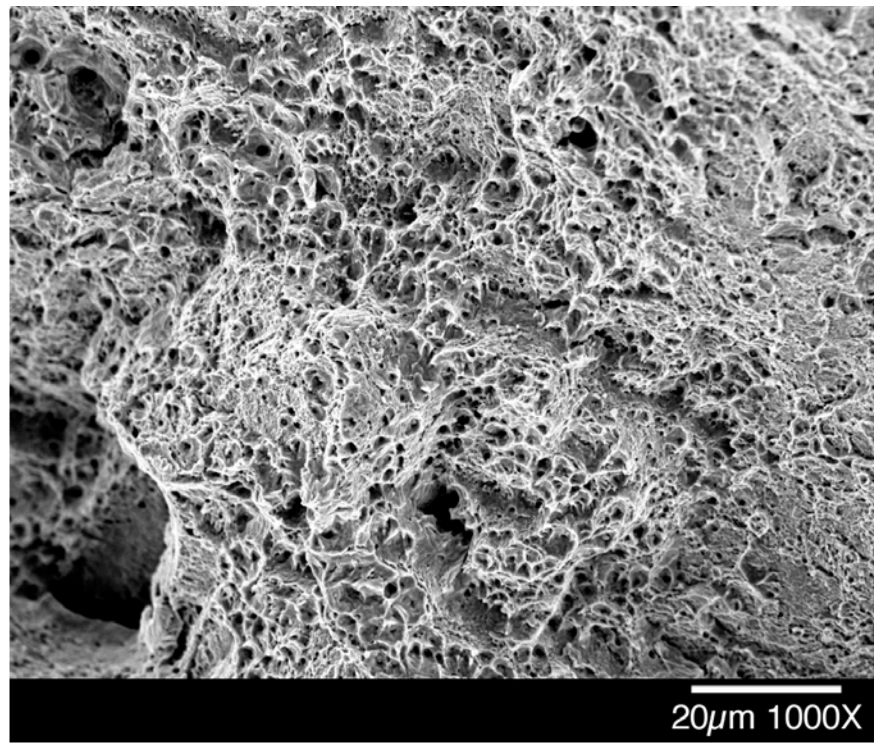
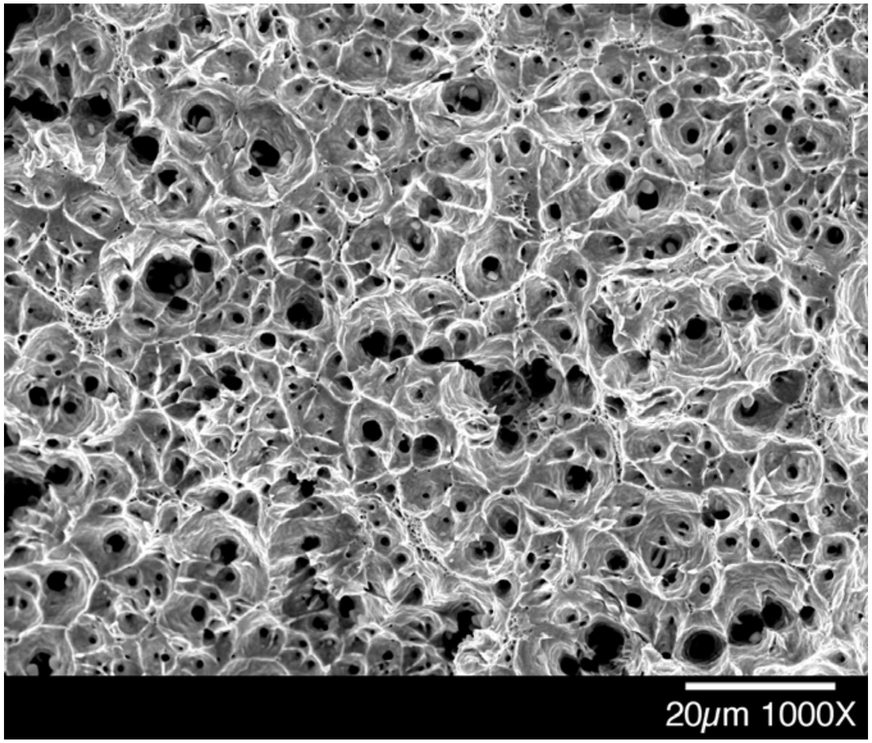


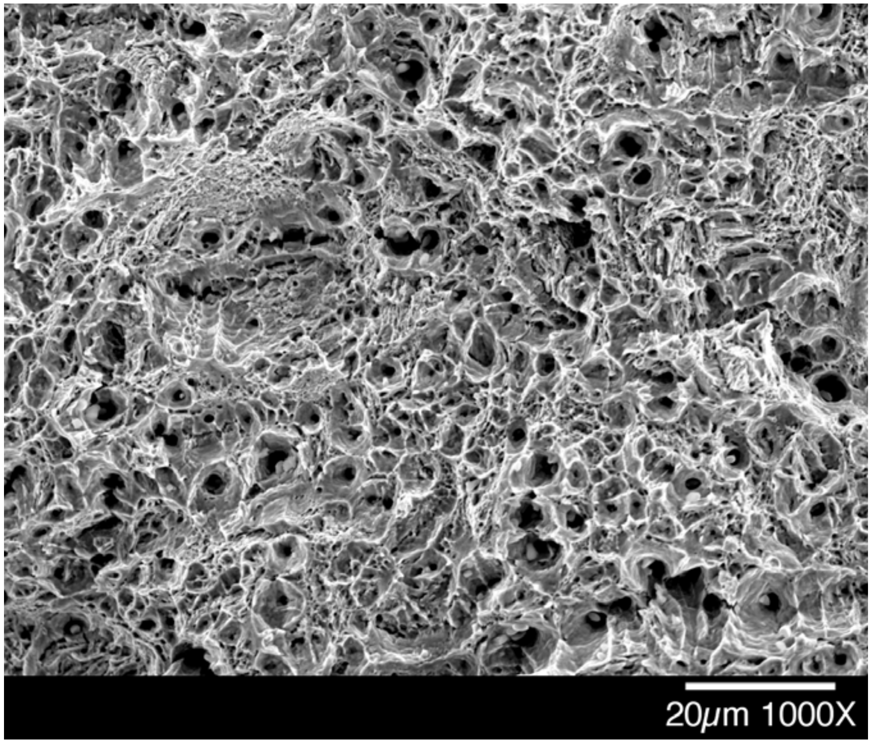
Thermally precharged

Fracture Surfaces: Tensile

316L, Cold-Worked Bar



uncharged



Thermally precharged

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Fracture toughness

Material	Condition	Yield Strength S_y (MPa)	J-integral Fracture Toughness J_Q (N/mm)	Tearing Modulus dJ/da (MPa)	Linear Elastic Fracture Toughness K_{JQ} † (MPa $m^{1/2}$)	Linear Elastic Plane-Strain Fracture Toughness K_{IC} (MPa $m^{1/2}$)
SAF 2507 Cold-worked bar	uncharged	988	370	830	280	—
	precharged	1208	16	20	60	48
316 Cold-worked bar	uncharged	563	190	400	210	—
	precharged	665	160	350	190	—
316L VIM/VAR Cold-worked bar	uncharged	594	310	500	260	—
	precharged	690	180	350	200	—
316L Cold-worked bar	uncharged	583	200	360	210	—
	precharged	694	120	270	160	—

† $K_{JQ} = \sqrt{J_Q E'}$ where $E' = 220$ GPa for SAF 2507 and $E' = 216$ GPa for 316 stainless steel.

Hydrogen precharging: 573K, 138 MPa hydrogen gas, 30 days.

SAF 2507: 125 wppm hydrogen (0.70 at%)

316 alloys: 136 wppm hydrogen (0.76 at%)

All specimens were precracked in fatigue. Testing was performed at room temperature in air.

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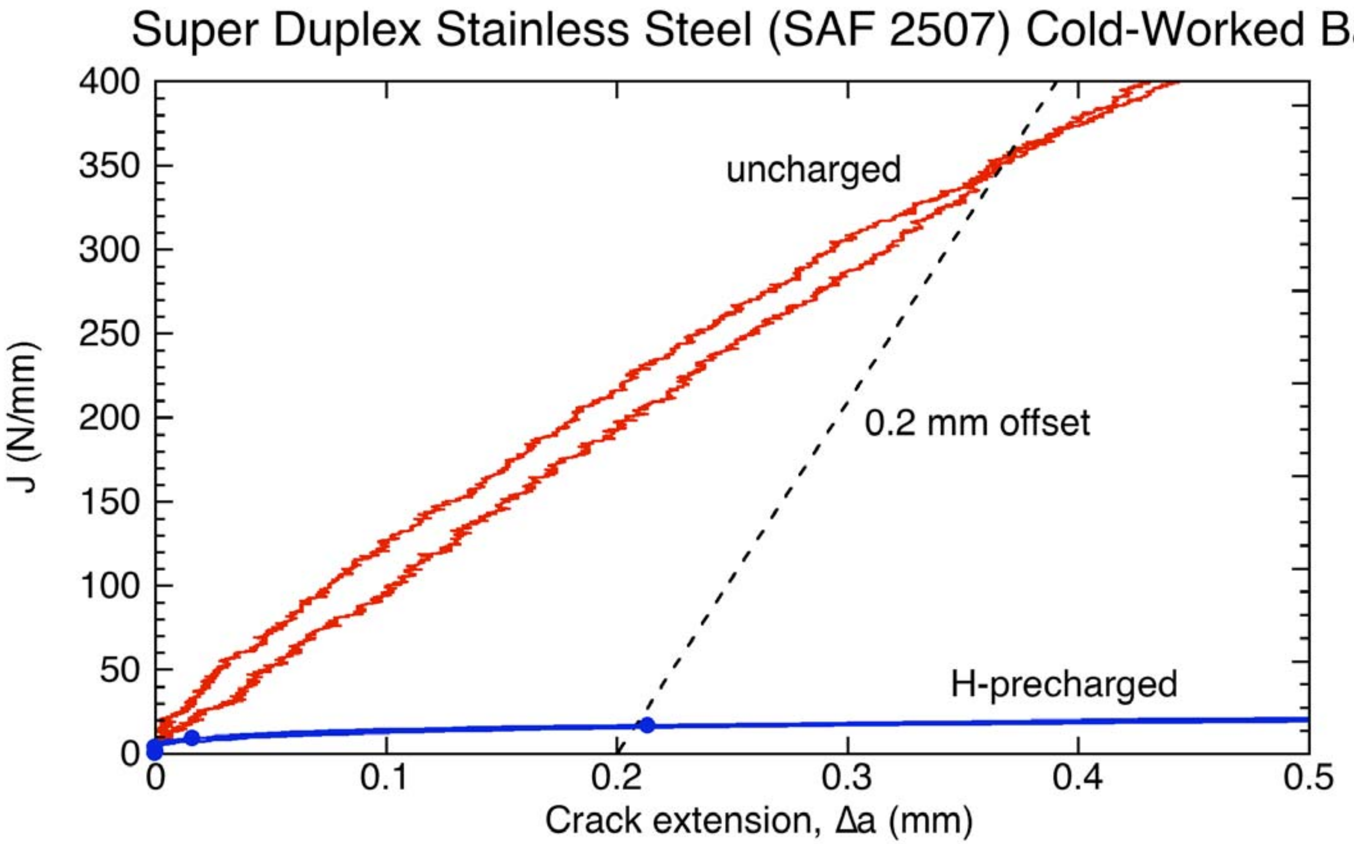
Fracture toughness

SAF 2507 Cold-Worked Bar



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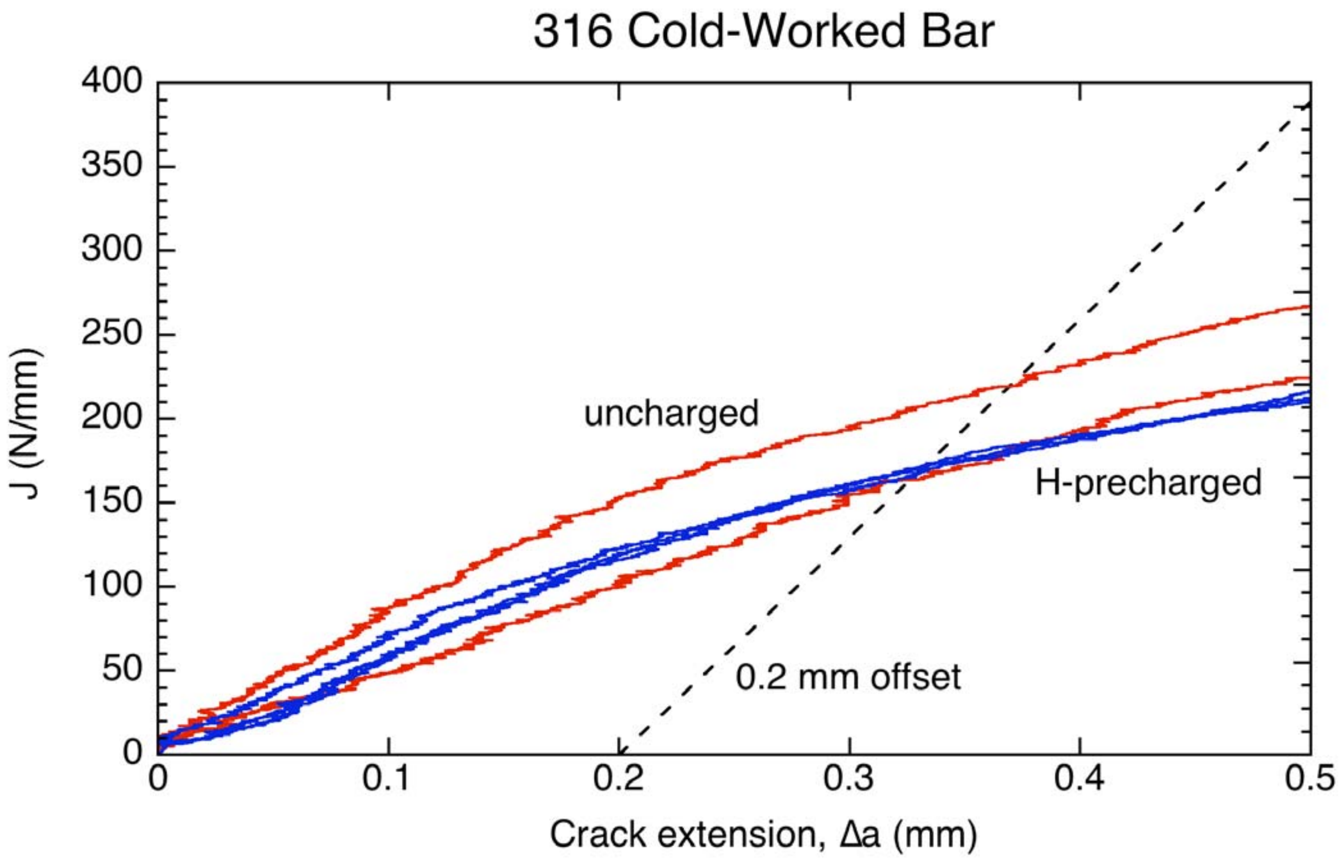
Fracture toughness

316 Cold-Worked Bar



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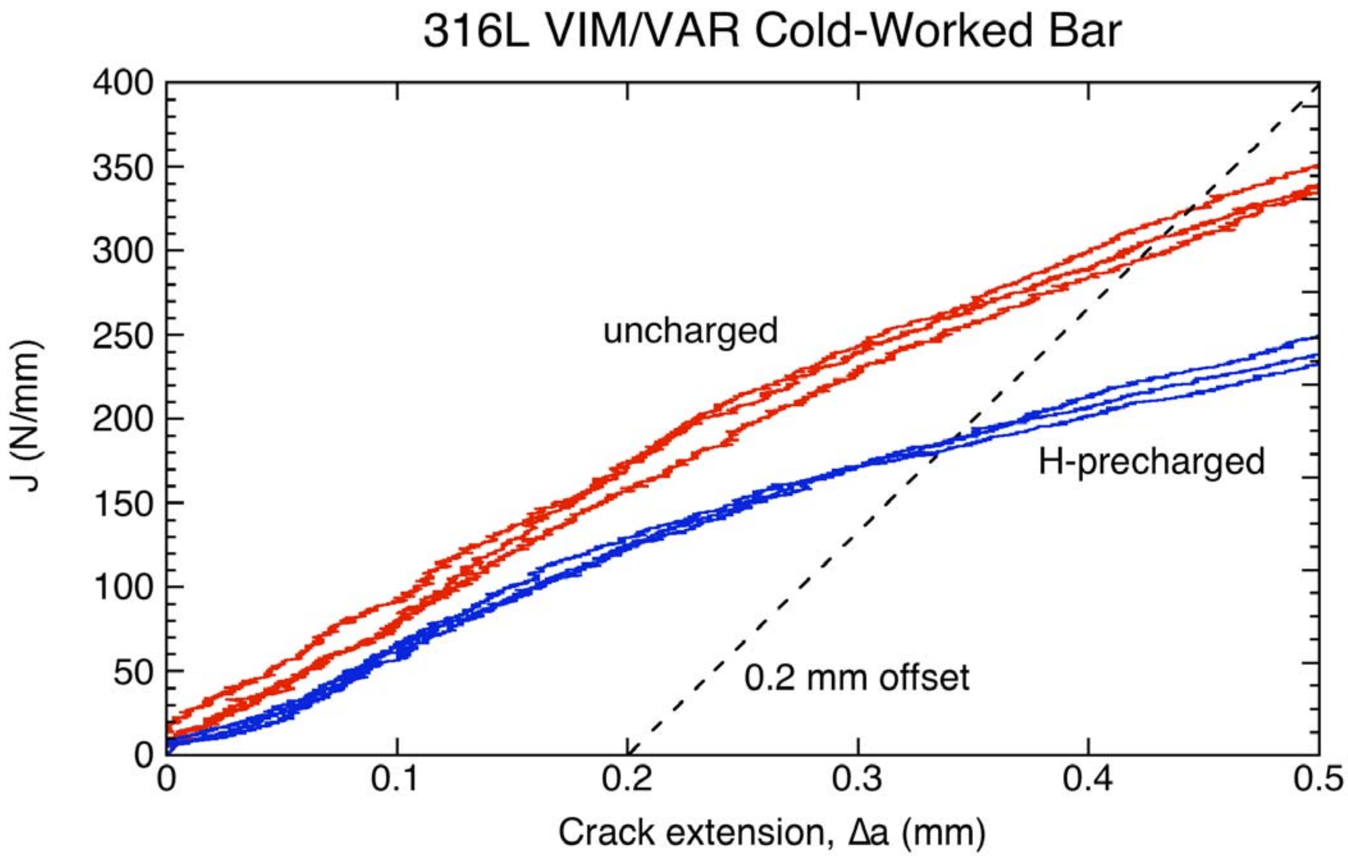
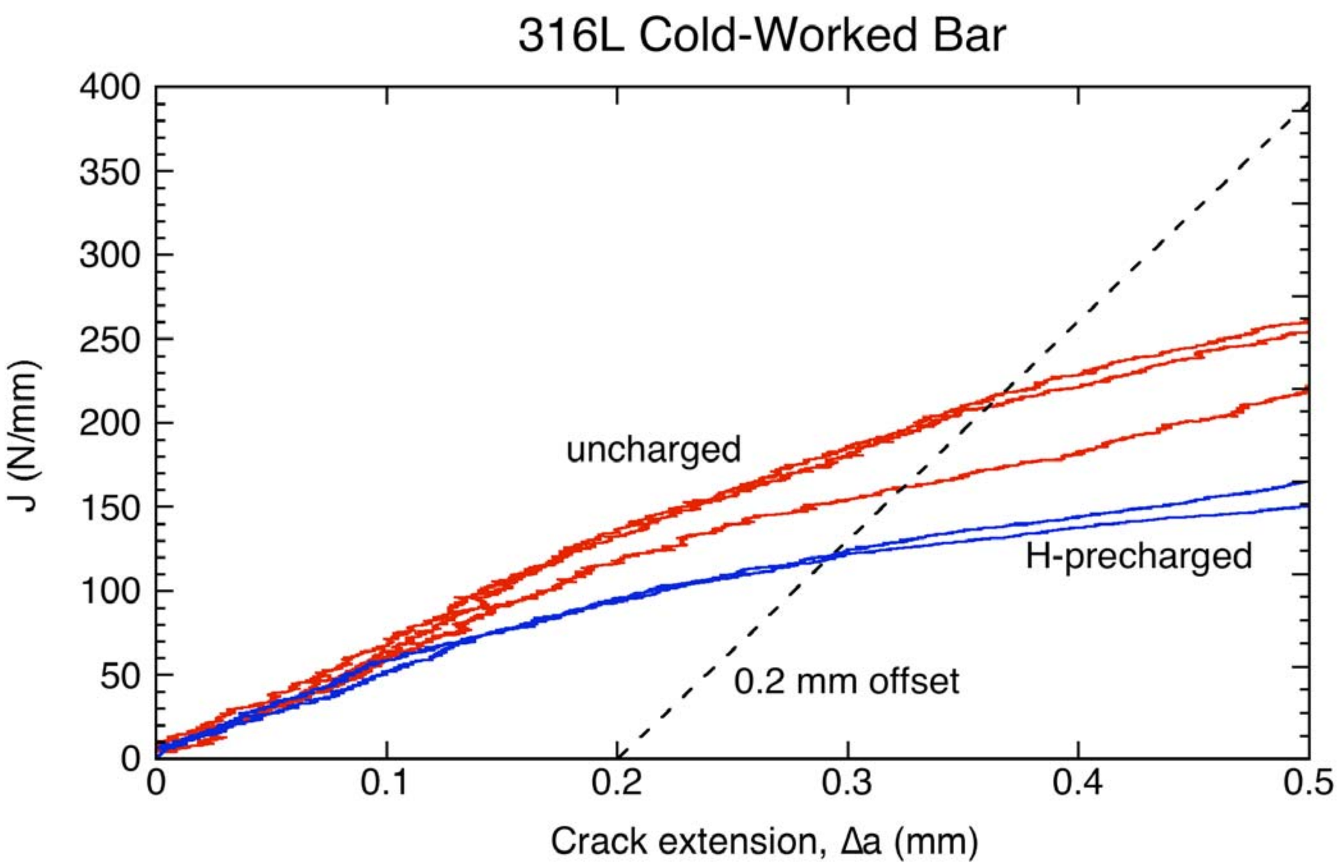
Fracture toughness

316L VIM/VAR Cold-Worked Bar



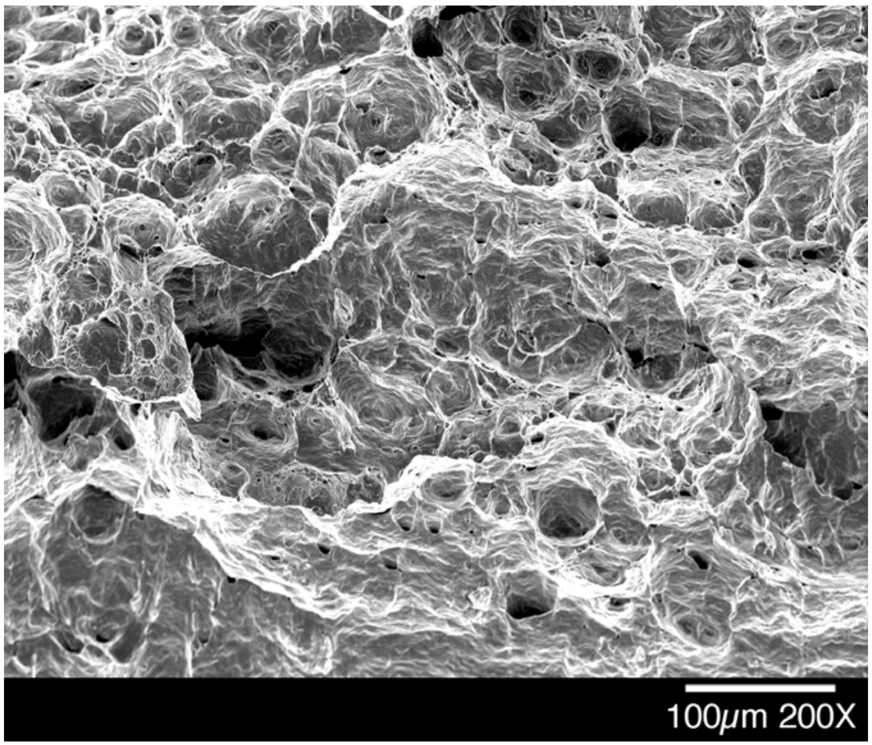
Fracture toughness

316L Cold-Worked Bar



Fracture Surfaces: Fracture Toughness

SAF 2507, Cold-worked Bar



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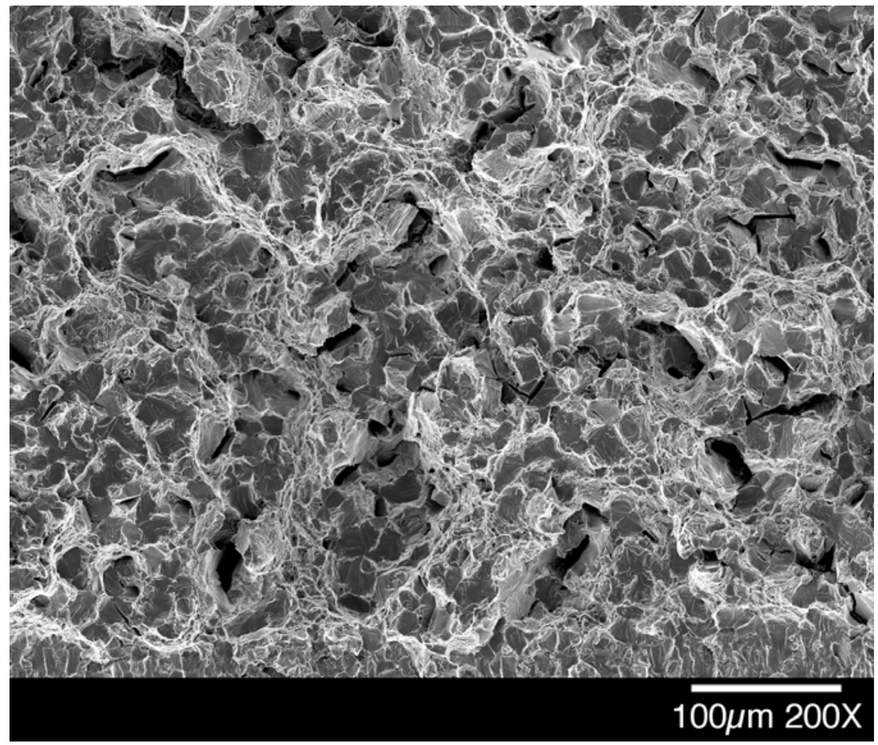
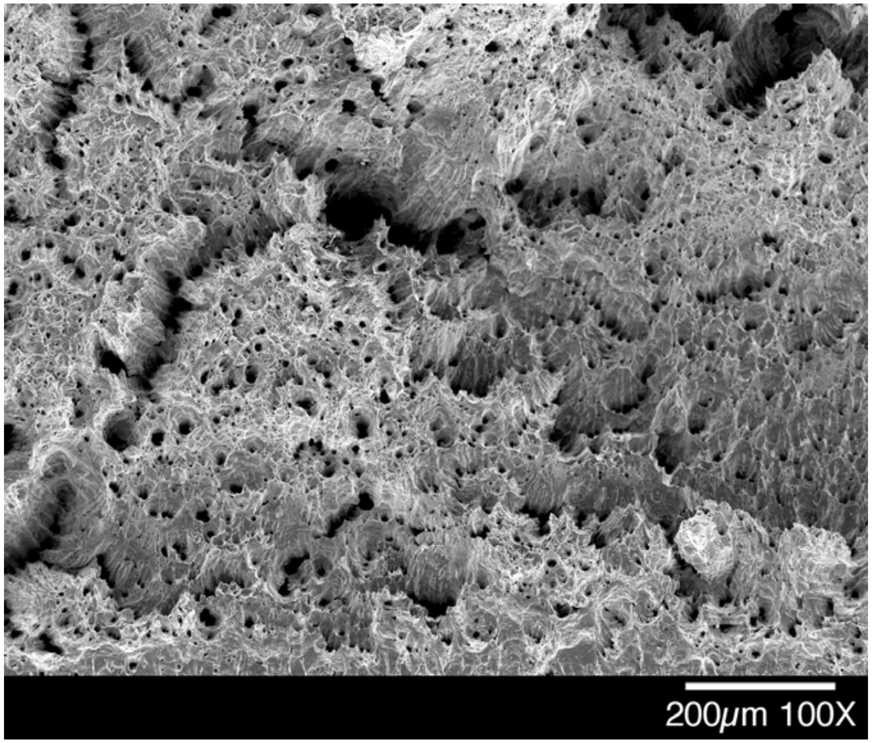


Thermally precharged

Fracture Surfaces: Fracture Toughness

316L, Cold-Worked Bar



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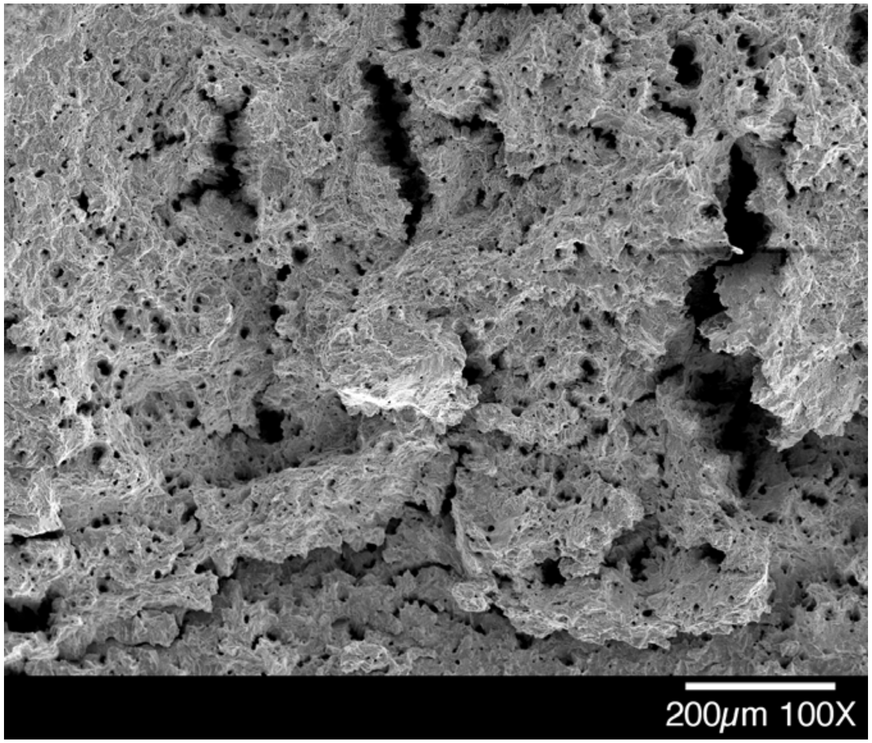

Thermally precharged

Conclusions

Super Duplex Stainless Steel, alloy SAF 2507

- SAF2507 is susceptible to hydrogen-assisted fracture
  - Significant decrease in ductility (RA) is displayed in tensile tests of specimens with internal hydrogen (thermally precharged) for both annealed and cold-worked condition
  - Change in fracture mode: with internal hydrogen, the ferrite phase appears to show cleavage fracture
  - Cold-worked microstructure is more susceptible to hydrogen effects
- Despite the reduction in ductility and change in fracture mode, SAF2507 in the annealed condition with internal hydrogen is nominally ductile in tension with an RA = 45%
- Fracture toughness was only measured for the cold-worked condition in the radial direction (SEB): $K_{IC} = 50$ MPa $m^{1/2}$
- The fracture morphology in the SEB specimens is similar to the tensile specimens with the addition of secondary cracking

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Conclusions

316 stainless steel alloys

- Modest reduction in ductility and increase in strength for all alloys with internal hydrogen
  - RA > 50% and total elongation ≥ 40% for all 316 alloys with internal hydrogen
  - Fracture mode of 316 alloys in tension nominally unchanged by hydrogen, although some changes in the morphology of fracture surface
- Geometry independent plane-strain fracture toughness was not obtained in this testing
  - The measured stress intensity factor (K_{JQ}) was ≥160 MPa $m^{1/2}$ for all tested cold-worked 316 alloys with internal hydrogen
  - Fracture toughness (J_Q) of cold-worked 316 alloys with internal hydrogen was reduced by as much as 40% compared to uncharged
- Cold-worked and annealed materials had similar resistance to internal hydrogen in tensile tests
- 316L VIM/VAR and 316 materials displayed similar resistance to hydrogen-assisted fracture in tensile tests
- 316L had the lowest nickel content (11wt%) of the three alloys and suffered the greatest reduction in ductility with internal hydrogen

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Acknowledgments

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