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Materials Performance at Liquid Hydrogen Temperatures

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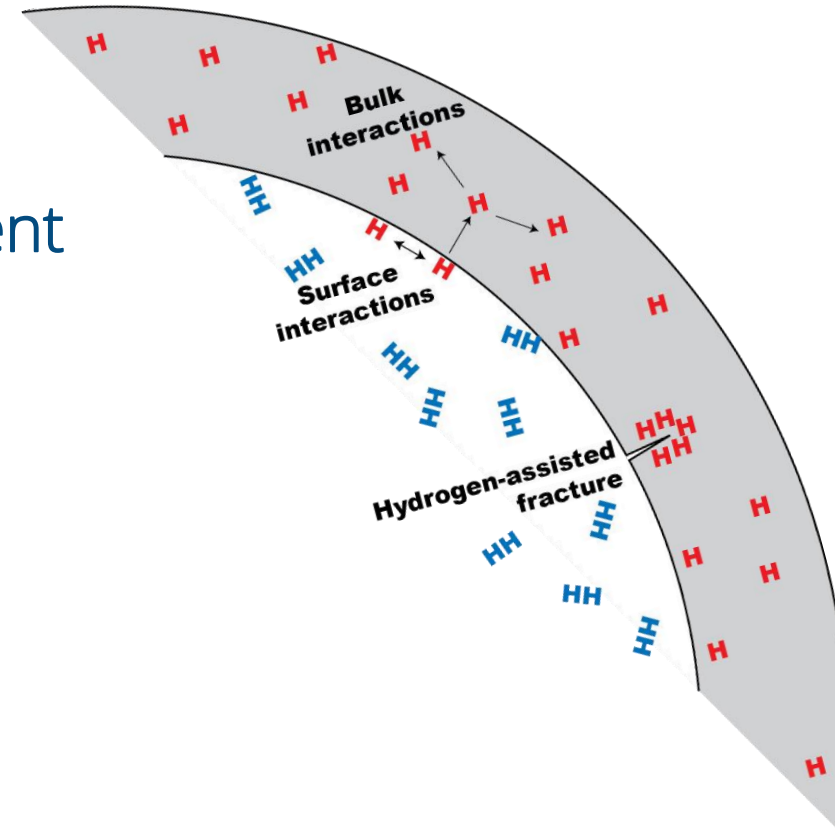
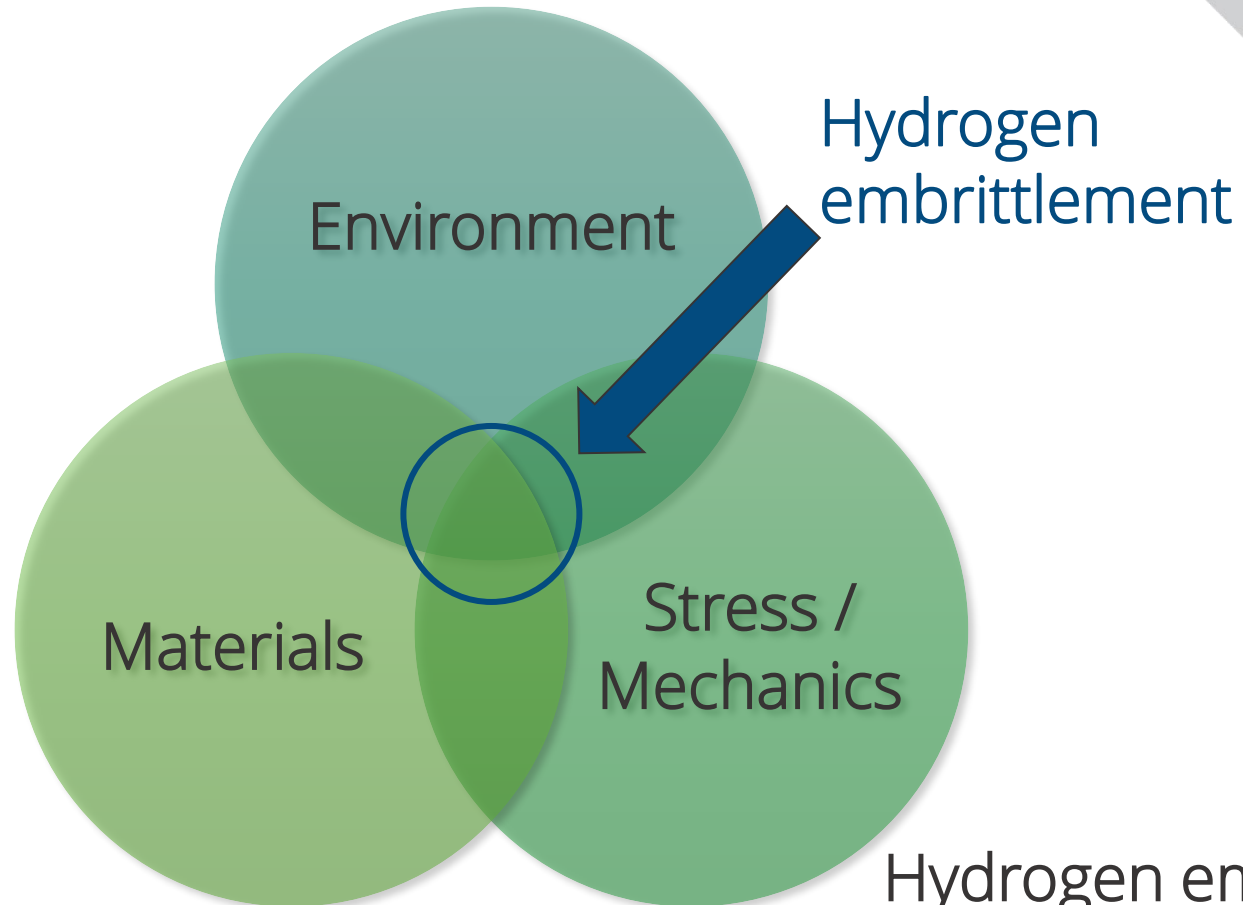
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Hydrogen embrittlement occurs in materials under the influence of stress in hydrogen environments



Hydrogen embrittlement occurs when hydrogen:

- 1) dissociates on metal surfaces
- 2) dissolves into the metal lattice
- 3) diffuses to regions of tensile stress



Conventional Cryogenic Materials for LH₂

3XX series austenitic stainless steel

- High toughness, high ductility, good performance in H₂
- 304N for trailer applications
 - N is nitrogen strengthened to allow reduced weight

Aluminum alloys

- Low sensitivity to hydrogen
- No DBTT (ductile to brittle transition temperature)
- Good when weight reduction is critical

~~Ferritic/Martensitic alloys~~

- 3.5, 5, 9 Ni-alloys are martensitic and have minimum temperature usages of 76 K



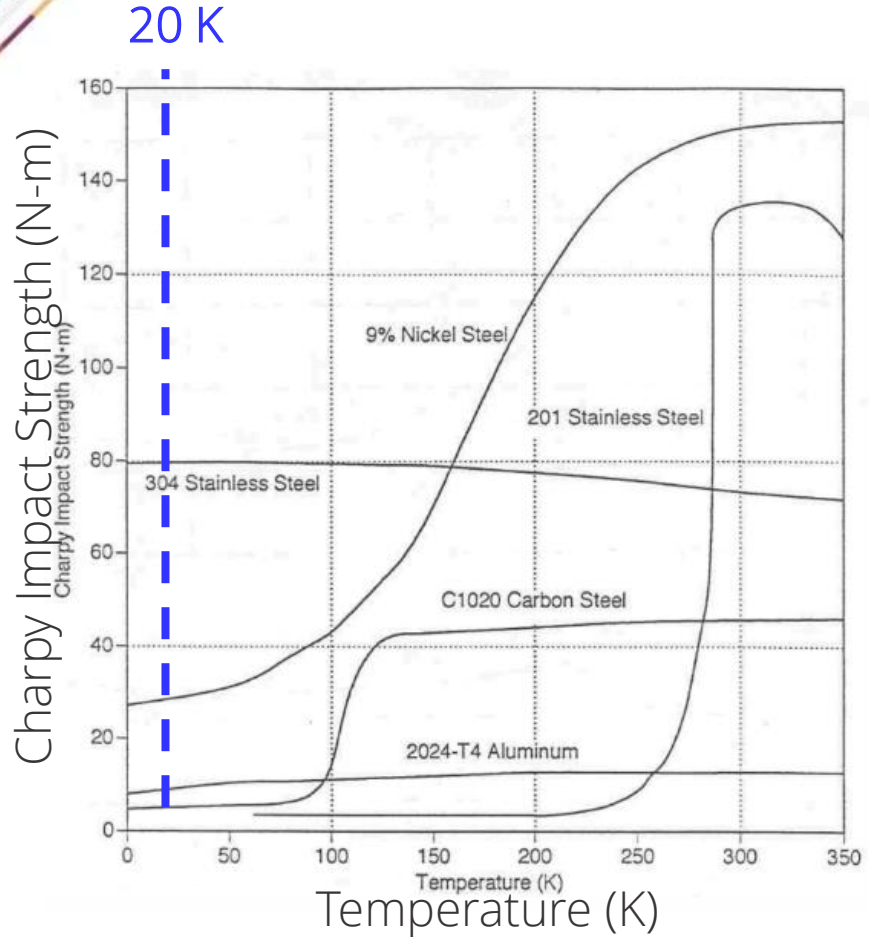
NASA 1950/1960s
Stainless steel

Not suitable for LH₂

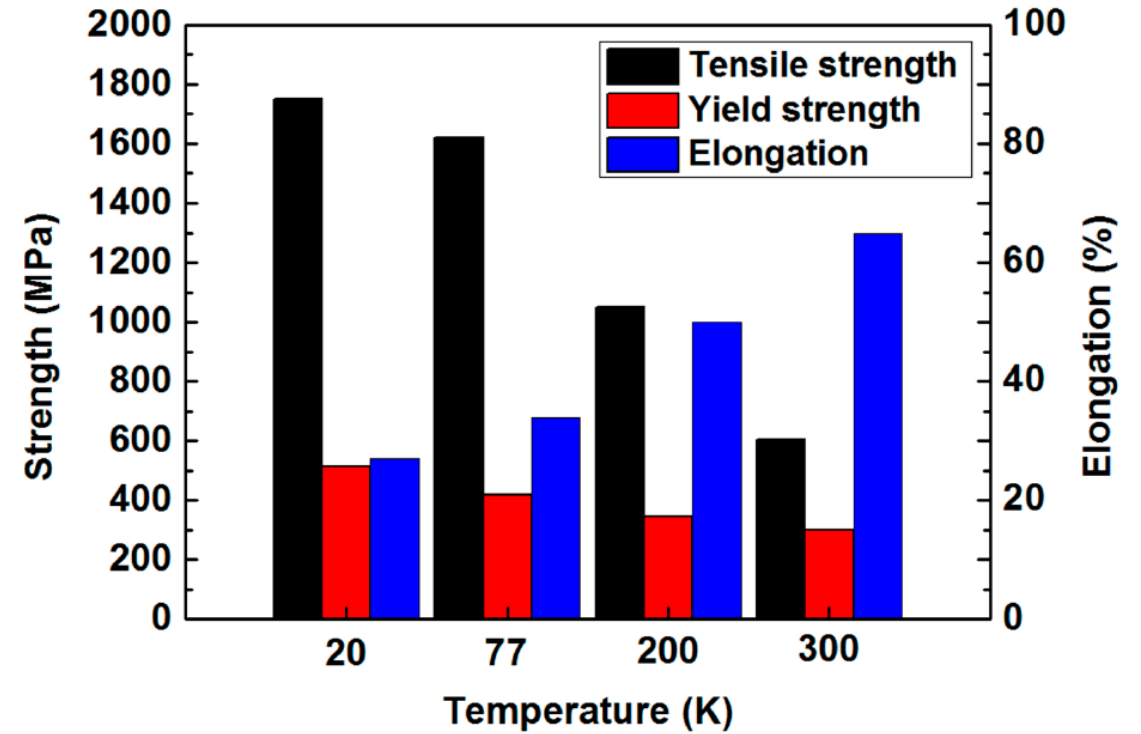
Alloys used at cryogenic temperatures must exhibit good toughness
→ For LH₂ use, high toughness must extend down to 20K.



Ductility decreases at cryogenic temperatures



From: NASA, Safety Guide for Hydrogen and Hydrogen System



Strength increases at lower temperatures;
Elongation to failure decrease

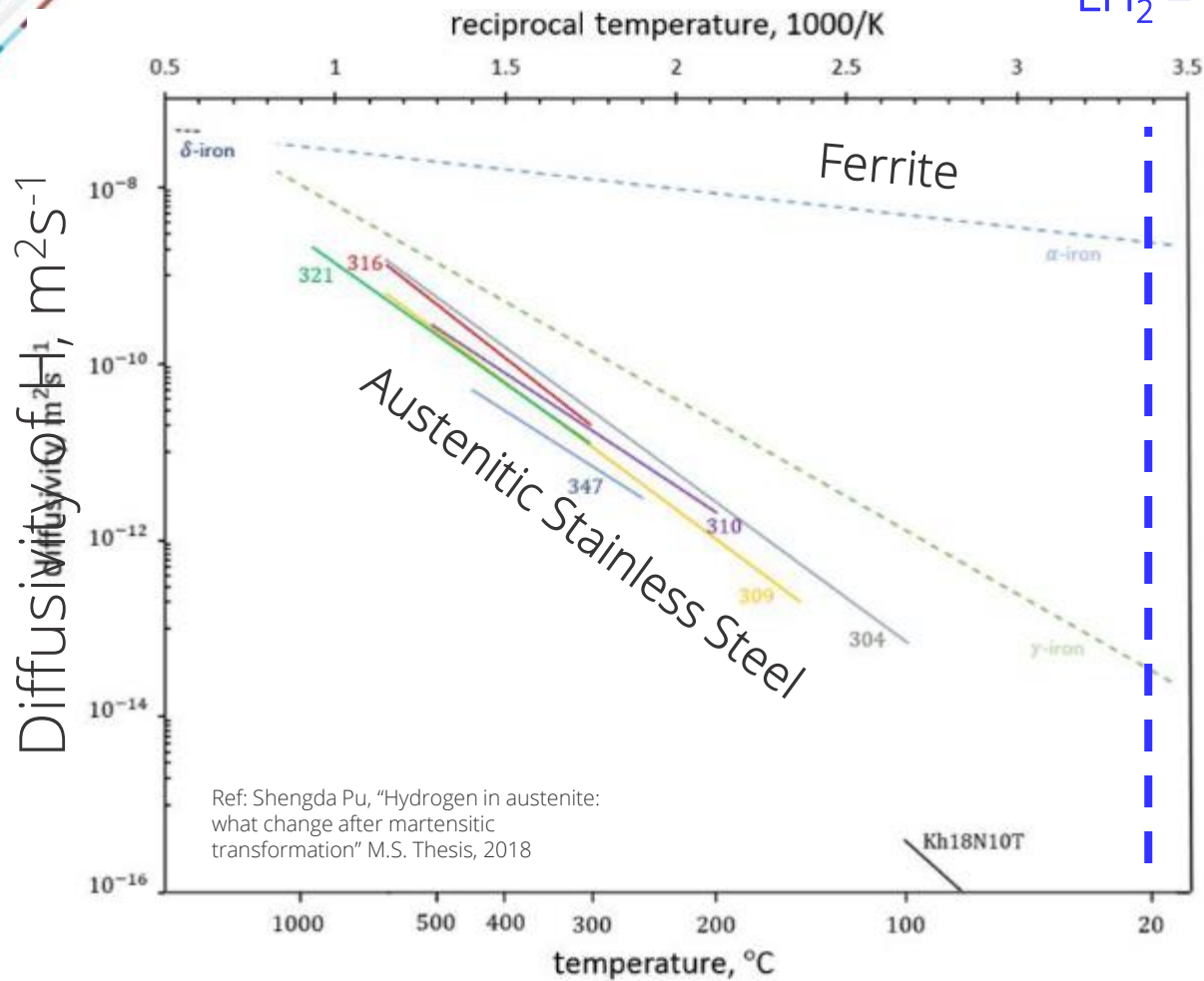
Ref: Cryogenic properties of 3XX series stainless steel at different temperatures (Qiu, *Metals* 2021)

Low-temperatures reduce ductility (elongation)
→ Hydrogen can further degrade mechanical properties

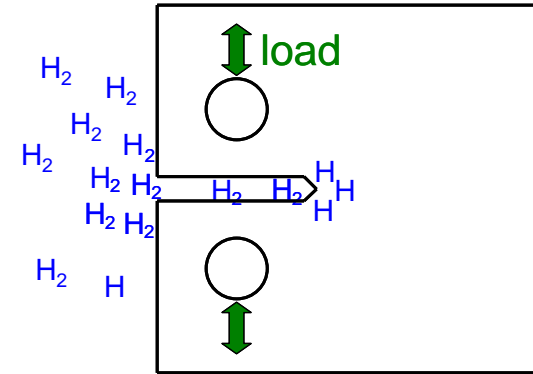


Cryogenic temperatures greatly limit hydrogen diffusion

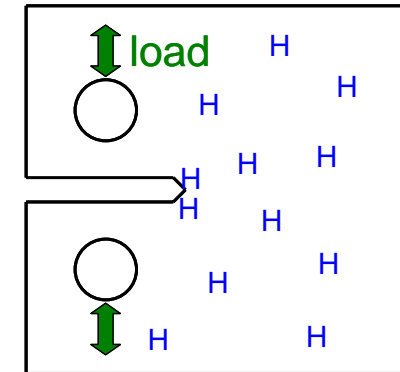
$L_{H_2} = 20 \text{ K}$



External Hydrogen Gas



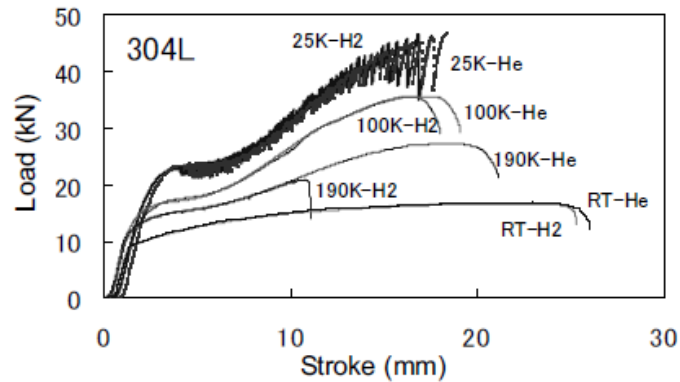
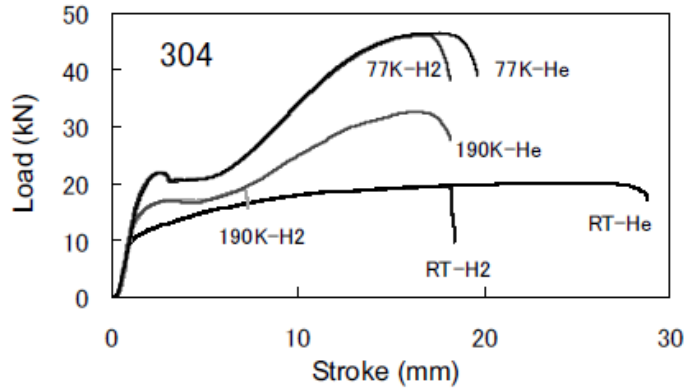
Hydrogen Precharged



Kinetics are important to consider and may influence test results
→ Experiments should try to mimic long-term exposures



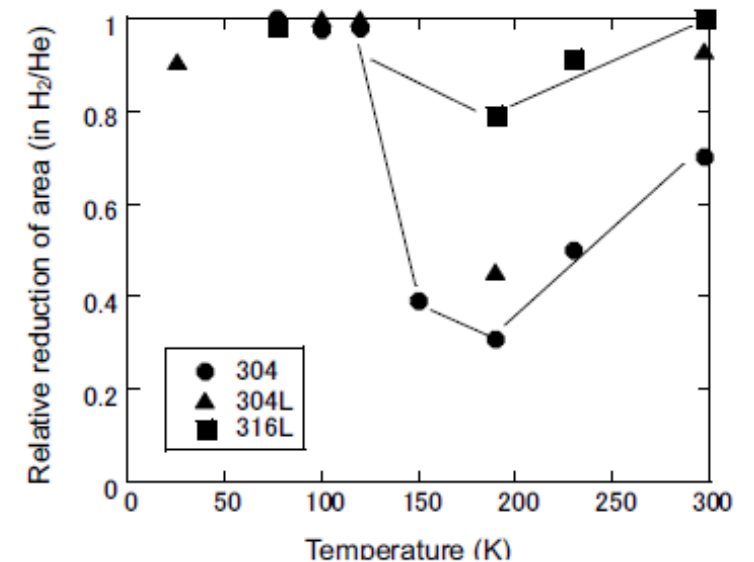
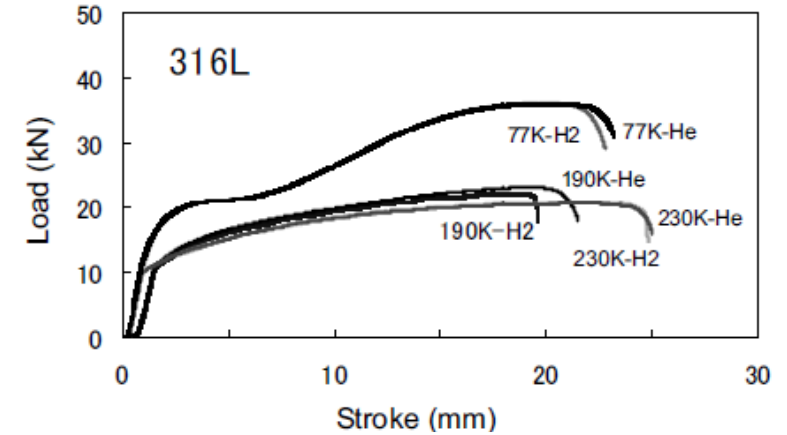
Ductility loss due to external gaseous H₂ appears to diminish at <100 K



External gaseous hydrogen

H₂ = 13 MPa H₂
He = 12 MPa He

Ref: T. Ogata, "Hydrogen embrittlement evaluation in tensile properties of stainless steels at cryogenic temperatures, AIP Conference 2008)
<https://doi.org/10.1063/1.2900335>

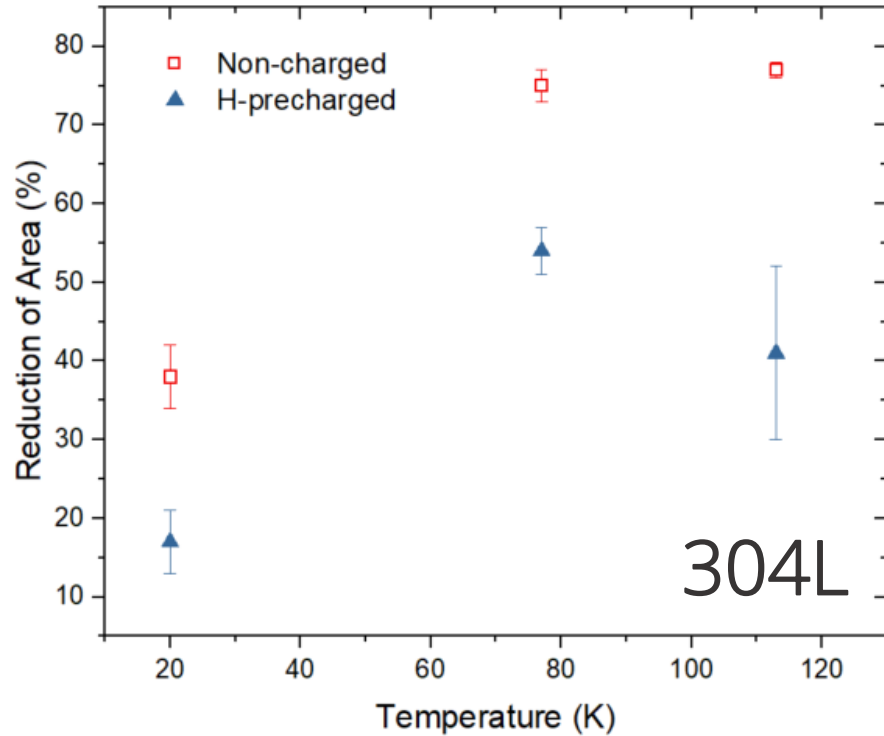


Metastable alloy (like 304) can transform to martensite due to strain and low temperatures.

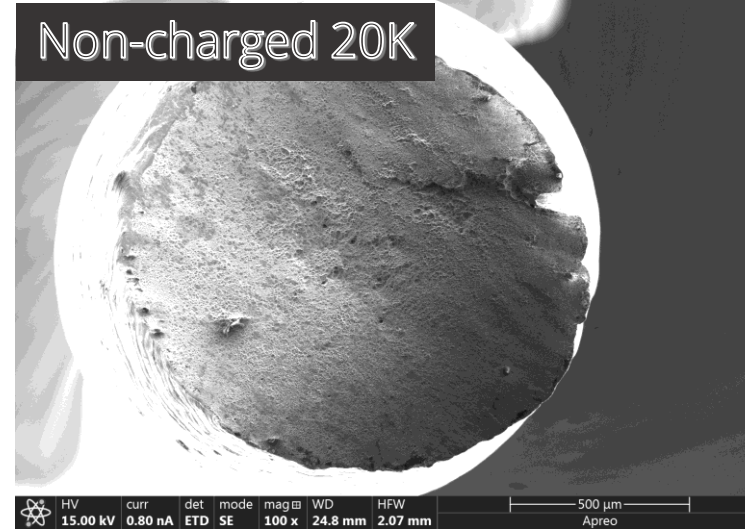
- Metastable austenitic stainless steels (304, 304L) exhibit greatest ductility losses in hydrogen gas in 150-230K range
- At <100K, negligible loss in ductility due to hydrogen – likely diffusion limited



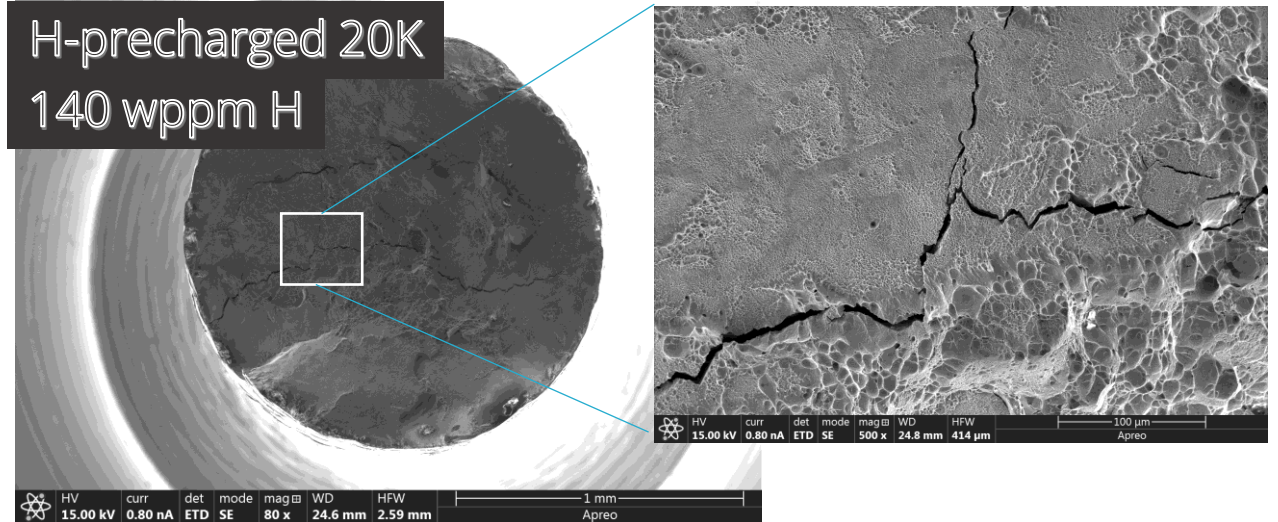
Precharged hydrogen reduces ductility (reduction of area)



(D. Merkel, "Effect of hydrogen on tensile properties of 304L stainless steel at cryogenic temperatures, PVP2021-62436)



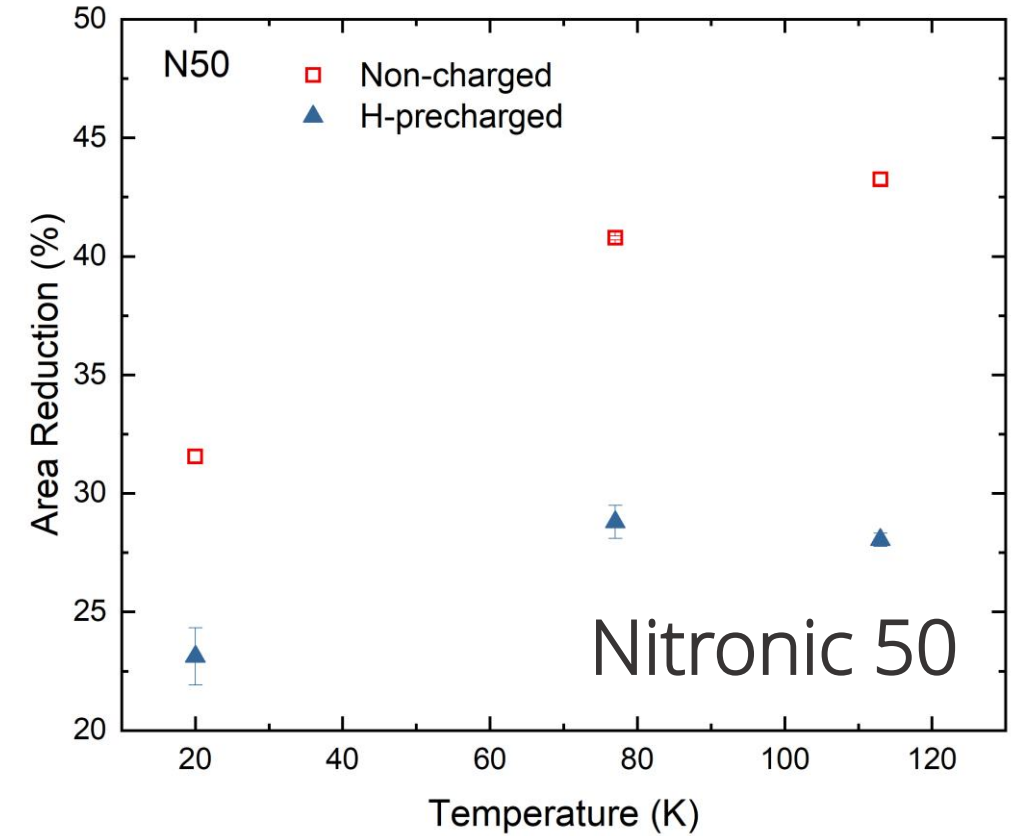
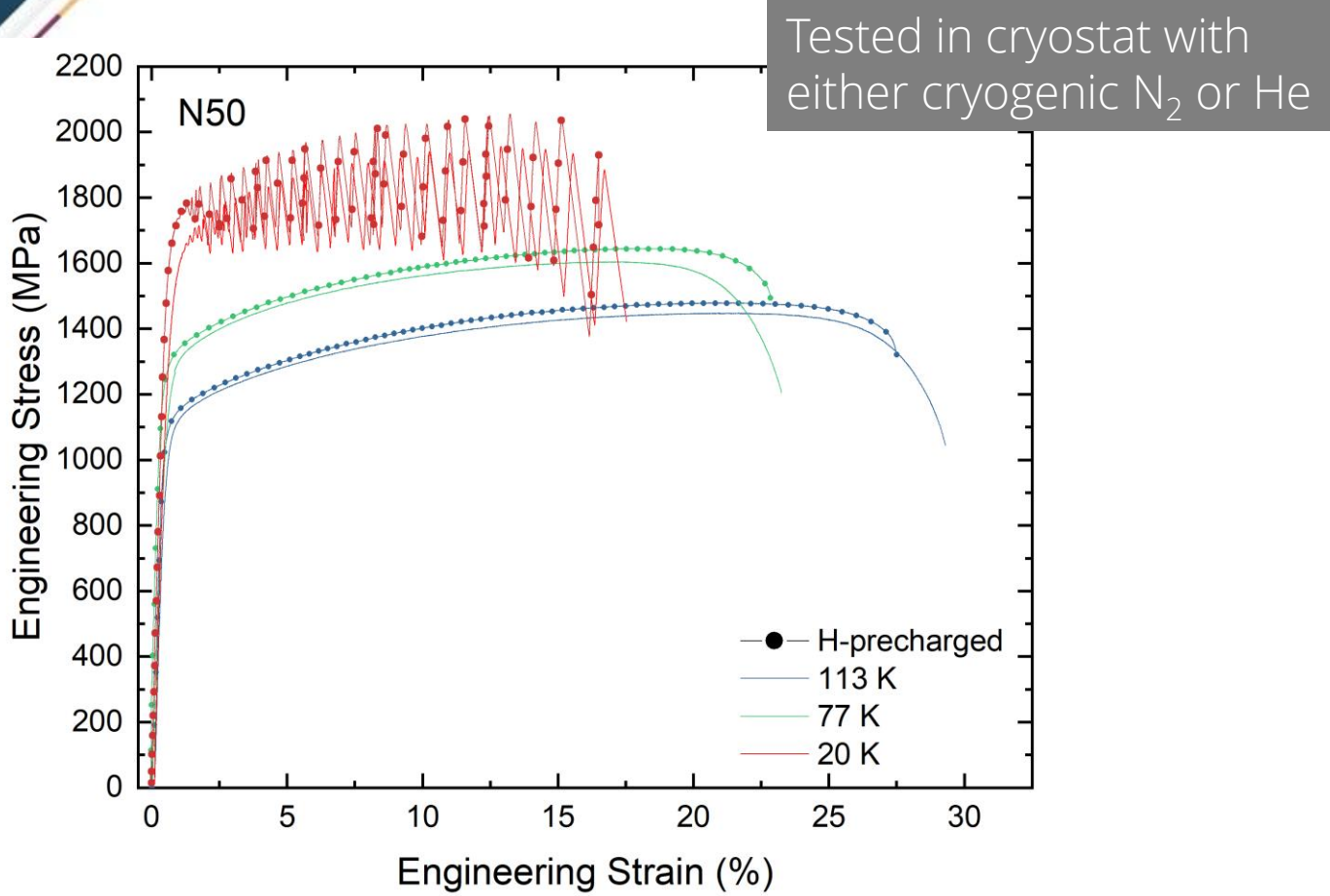
Tested in cryostat with either cryogenic N₂ or He



Reduction of area consistently lower in H-precharged samples down to 20 K
→ Hydrogen can degrade 304L even at 20 K



Alternative austenitic stainless steels Nitronic 50 (XM-19) exhibit similar behavior to 304L

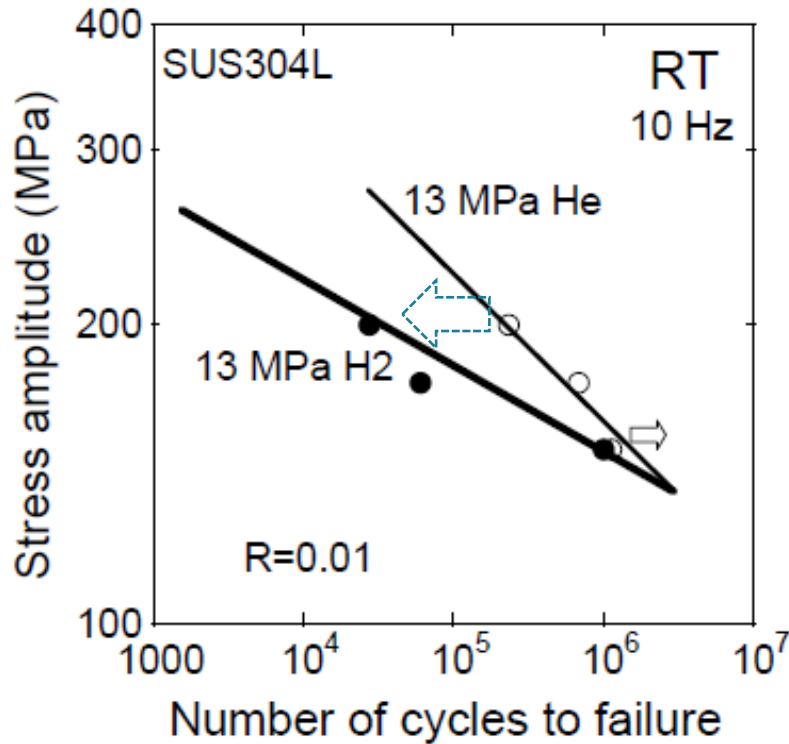


(D. Merkel, "Effect of hydrogen on tensile properties of stainless steel at cryogenic temperatures," MRS Fall 2021.

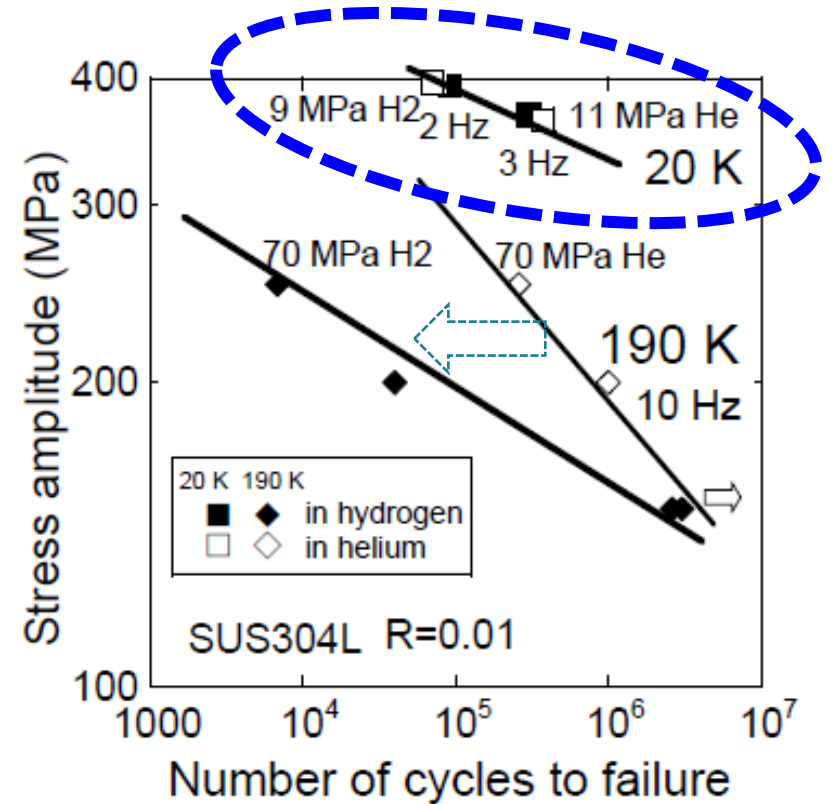
XM-19 offers higher strength alternative to 304L, but with similar effects due to H₂ at 20 K



Fatigue degradation due to H₂ diminished at 20K in lab tests



External gaseous hydrogen



At 293K, decrease in fatigue life due to H₂

At 190K, decrease in fatigue life due to H₂
At 20K, negligible difference between He and H₂

Ref: T. Ogata, "Hydrogen environment embrittlement evaluation in fatigue properties of stainless steel SUS304L at cryogenic temperatures, AIP Conference 2010) <https://doi.org/10.1063/1.3402310>

→ At 10 Hz, Hydrogen reduces fatigue life at 293K and 190K, no measured effect at 20K

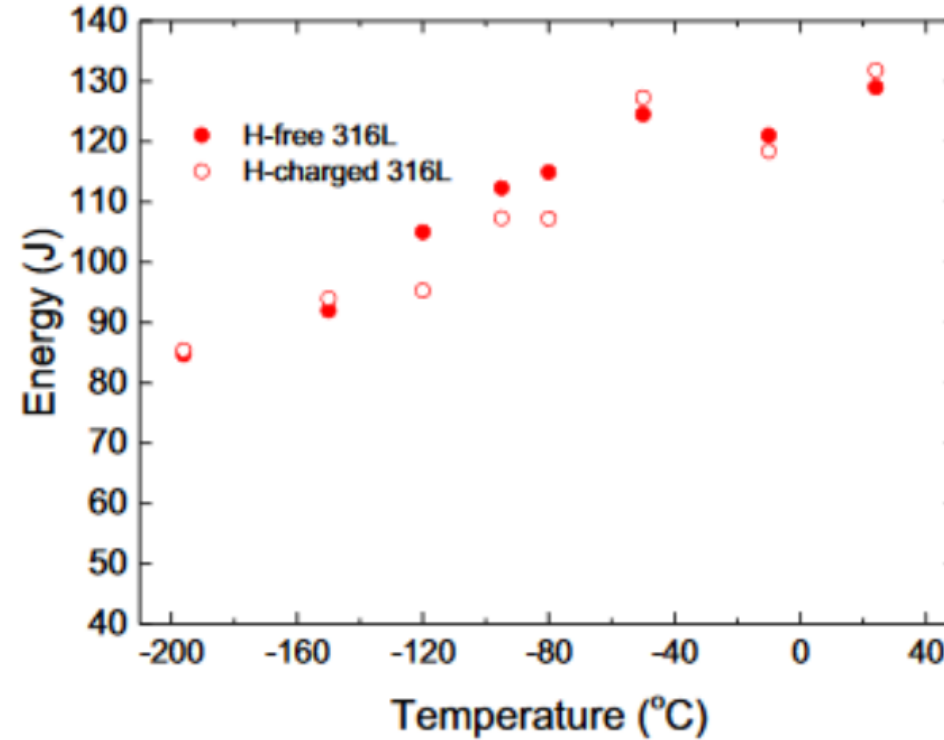
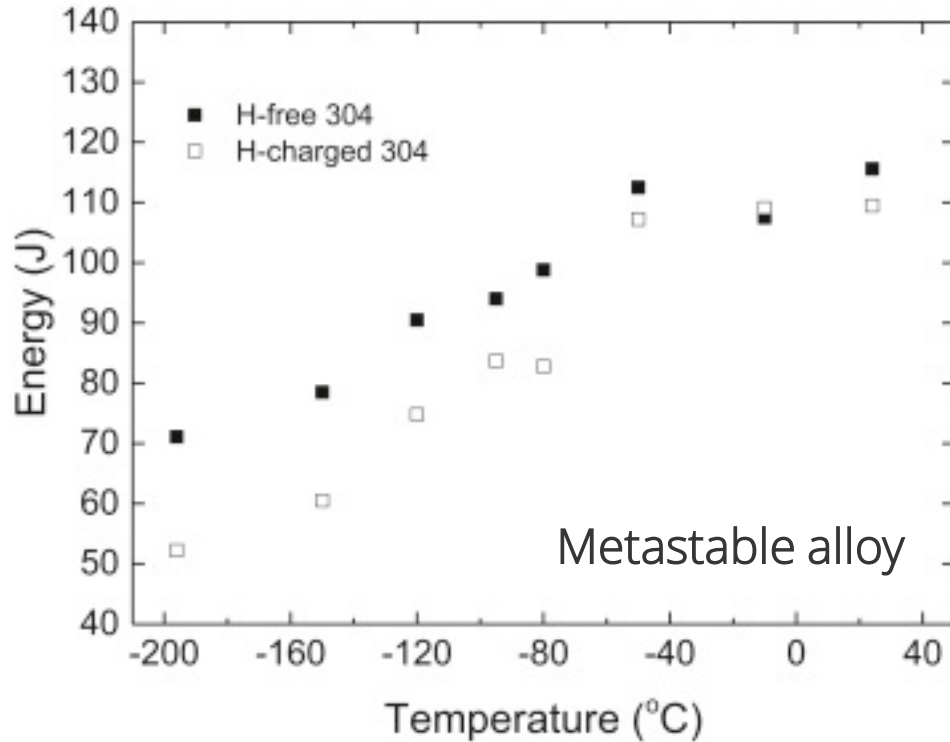
Fatigue load frequency in application is likely less than 10 Hz allowing more time for H-diffusion.
→ May result in different behavior



Charpy impact toughness of H-precharged austenitic stainless steels decreases in metastable alloys



Charpy impact test



, Low temperature tensile and impact properties of hydrogen-charged high manganese steel, *IJHE*, 2019.

Metastable = more likely to form martensite

→ Martensite is more susceptible to low temperature embrittlement and hydrogen embrittlement

Despite fast loading rates, hydrogen still can have a measurable impact at low temperatures



Summary

- Austenitic stainless steels (304/316) are used at cryogenic temperatures due to high toughness
 - At cryogenic temperatures, strength improves but ductility and impact toughness are reduced
- Most of material degradation is due to extreme low temperatures
 - Hydrogen can further degrade mechanical properties
 - Research on Nitronic 50 (XM-19) shows comparable tensile behavior to 304L
- Hydrogen diffusion is limited at 20 K which can affect laboratory tests
 - Important to consider when assessing long-term effects in applications
 - Precharged hydrogen can overcome slow diffusion and better represent long-term exposure
 - Slow rate fracture testing at low temperature is notable gap in literature



Thank you for your attention!

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References:

- Cryogenic properties of 3XX series stainless steel at different temperatures (Qiu, *Metals* 2021)
- NASA, Safety Guide for Hydrogen and Hydrogen System
- Shengda Pu, "Hydrogen in austenite: what change after martensitic transformation" M.S. Thesis, 2018
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