"The Benefits and Challenges with On-board Liquid Hydrogen Storage Systems"

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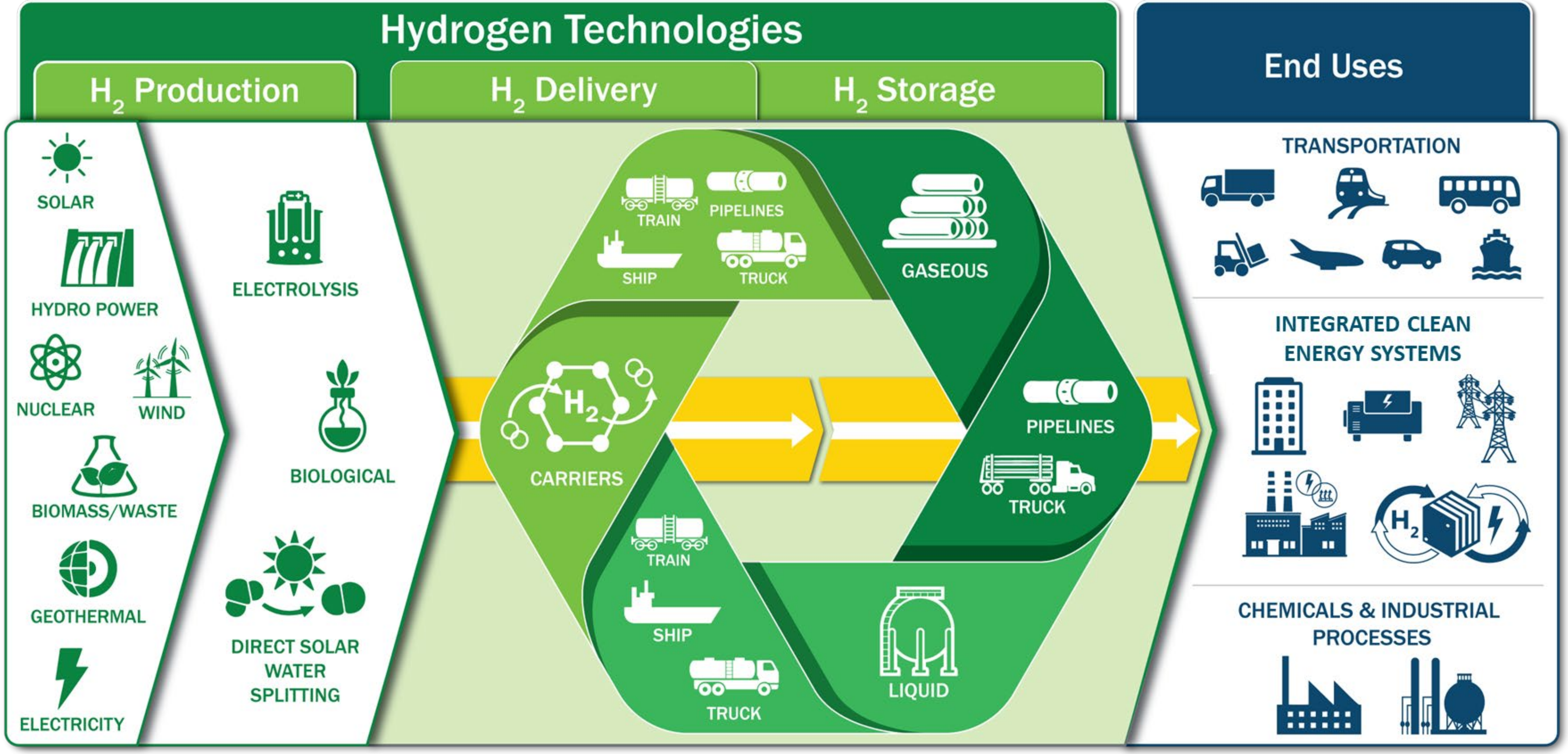
Outline

- DOE Goals
- Medium- and Heavy-Duty Vehicle On-board Storage
- Compressed Gas versus cryo-Compressed versus LH2
- Pressure and Temperature Fatigue
- Material challenges
  - Polymers
  - Composites
  - Metals
    - ✓ Welds
- Summary

DOE-Hydrogen Fuel Cell Technologies Office is accelerating H_2 technologies for decarbonization



Source: Ned Stetson 2021 Annual Merit Review HFTO

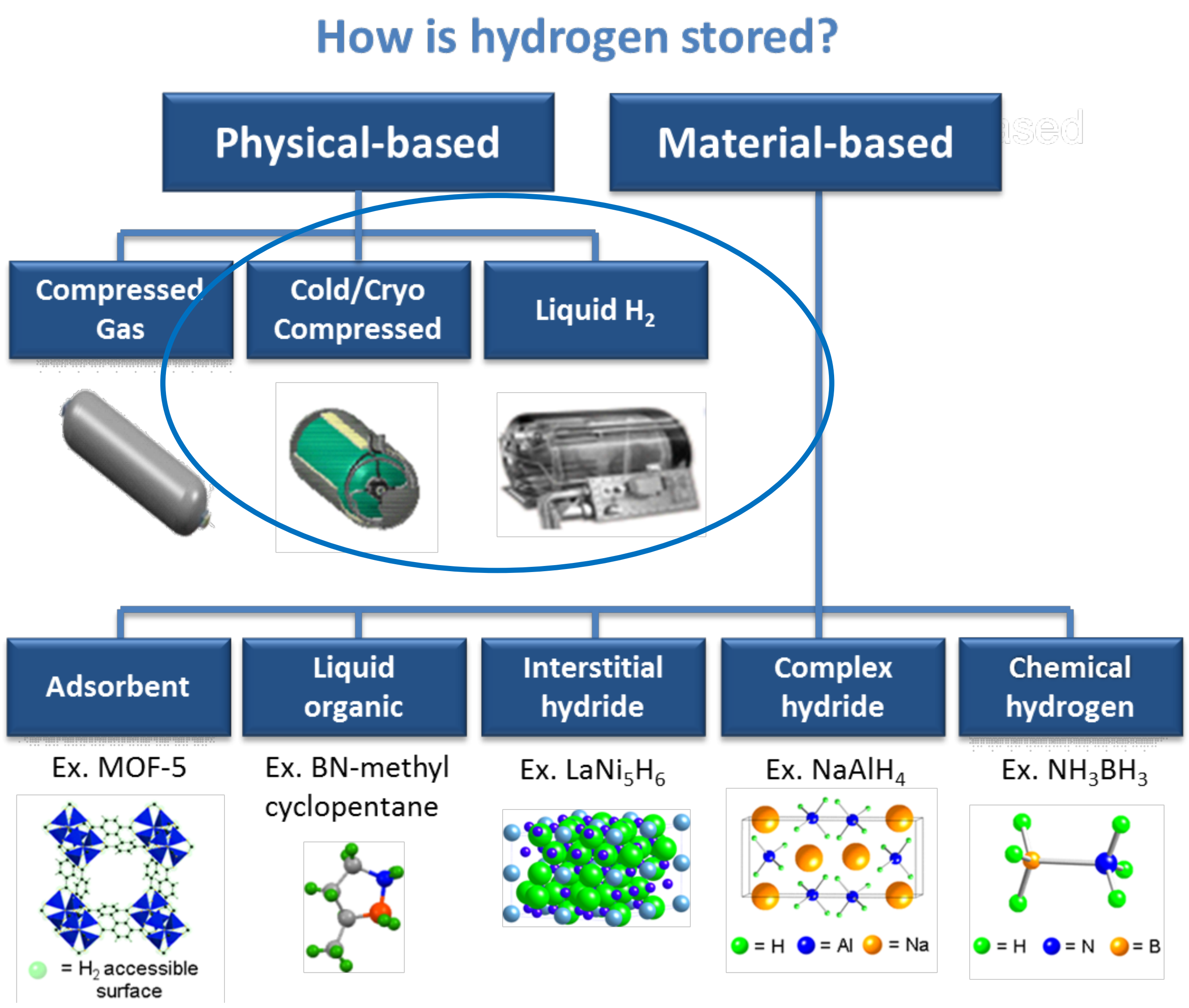
Pacific Northwest NATIONAL LABORATORY

Motivations

- DOE Hydrogen and Fuel Cell Technology Office
  - Targeting MD/HD vehicles
  - Requiring onboard storage capacities of 20-100 kgs
  - Constraints on weight and volume
- H_2 can be stored as gas or liquid
  - High-pressure Storage
    - ✓ 350 to 700 bar
    - ✓ Multiple tanks to achieve on-board storage

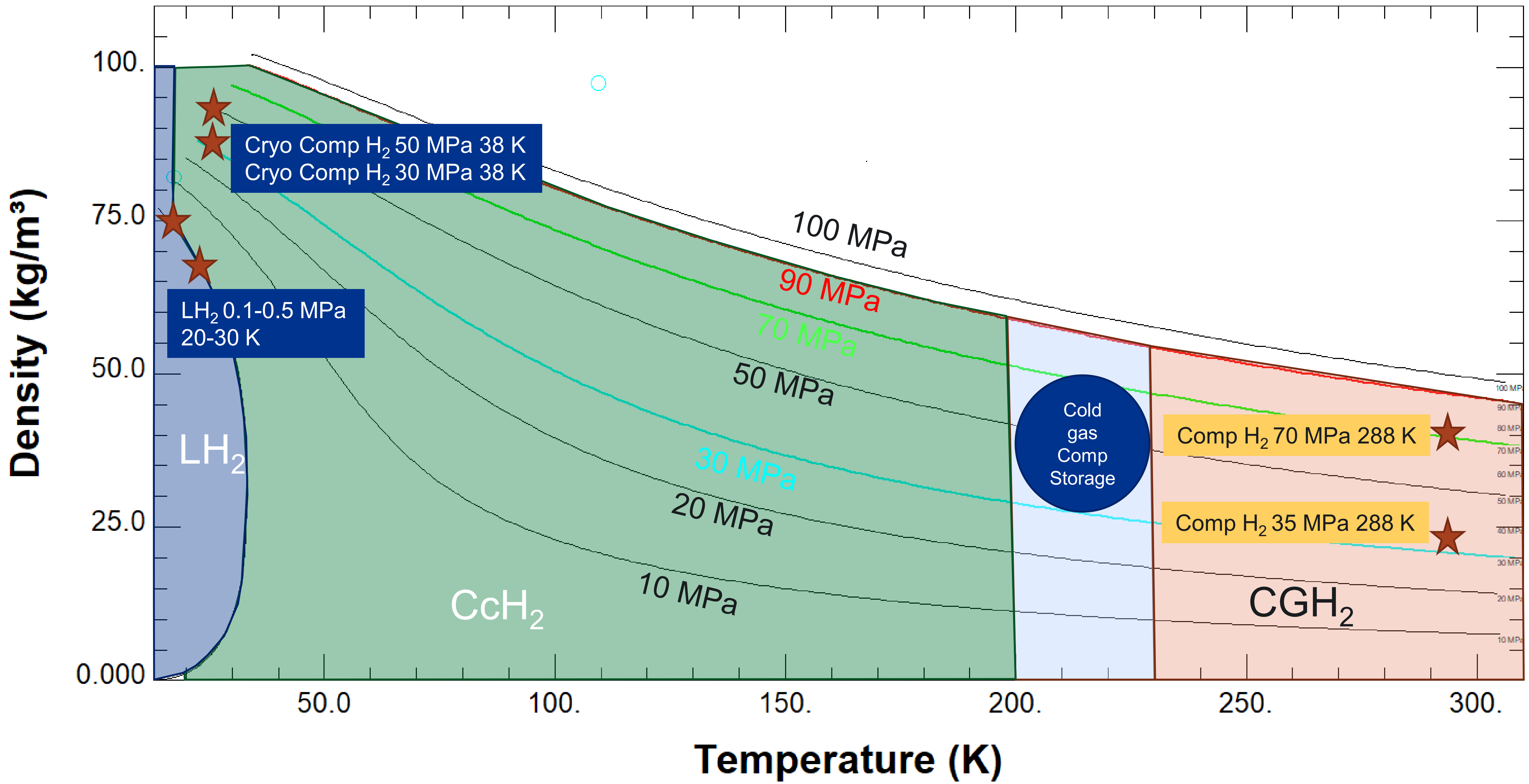
Insulated Systems

  - Cold/Cryogenic Compressed Storage
    - ✓ 350 to 500 bar
    - ✓ 200 K or 30-80 K
  - Liquid Hydrogen Storage
    - ✓ <10 bar
    - ✓ -253˚C (20 K)



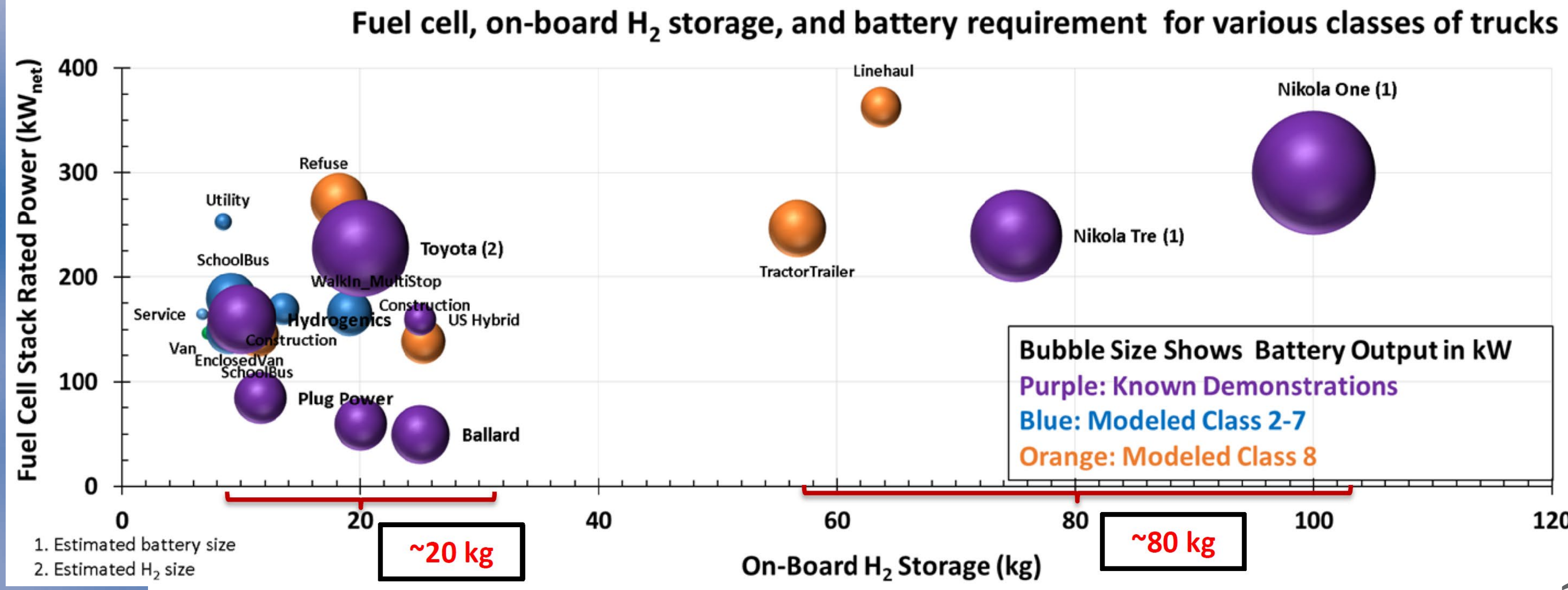
https://www.energy.gov/eere/fuelcells/hydrogen-storage

Hydrogen Regions of Interest for Storage



LH2 Liquid Hydrogen	CcH2 Cryo Compressed Hydrogen	CGH2 Compressed Gaseous Hydrogen

DOE Goals and Targets



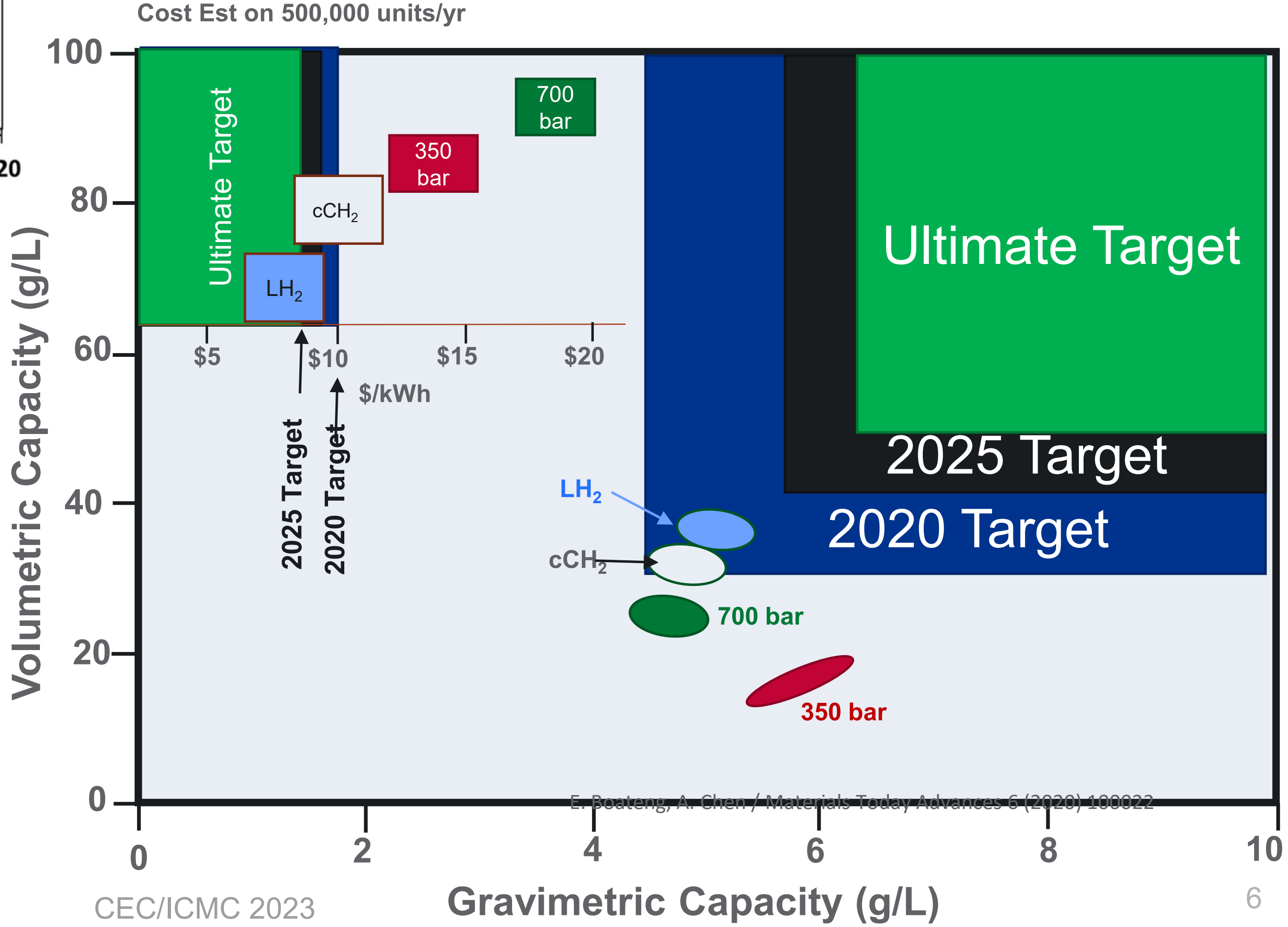
https://www.hydrogen.energy.gov/pdfs/review19/st100_james_2019_o.pdf

	Light-Duty Vehicle	Cold Gas Storage	Medium-Duty Vehicle	Heavy-Duty Vehicles	Cryo compressed	Liquid Hydrogen
Hydrogen Mass (kg)	5.6	5.6 k	20 kg	80 kg	80 kg	80 kg
Pressure (bar)	700	500	700	700	500	<10
Temperature	293K	200 K	293K	293K	50-80 K	20 K
Liner Materials	HDPE	HDPE	HDPE	HDPE	Metallic Al or SS	SS
Insulation					MLI	MLI
Outer shell					Metallic Al or SS	SS

3 Target Tables for Hydrogen Fueled Long-Haul Trucks

Table 1. Technical System Targets: Class 8 Long-Haul Tractor-Trailers (updated 10/31/19)

Characteristic	Units	Targets for Class 8 Tractor-Trailers	
		Interim (2030)	Ultimate[9]
Fuel Cell System Lifetime[1,2]	hours	25,000	30,000
Fuel Cell System Cost[1,3,4]	\$/kW	80	60
Fuel Cell Efficiency (peak)	%	68	72
Hydrogen Fill Rate	kg H_2/min	8	10
Storage System Cycle Life[5]	cycles	5,000	5,000
Pressurized Storage System Cycle Life[6]	cycles	11,000	11,000
Hydrogen Storage System Cost[4,7,8]	\$/kWh (\$/kg H_2 stored)	9 (300)	8 (266)



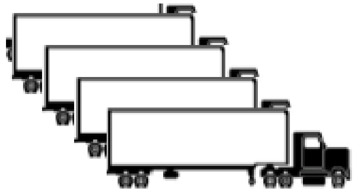
Liquid hydrogen's high density provides fewer truck transports compared to compressed hydrogen

Compressed Hydrogen[1]

4

275 bar, composite[2]

1,152 kg H_2 capacity/tanker



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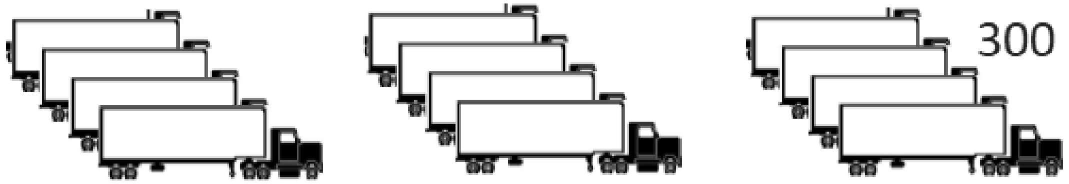
160-190 bar, steel

300 kg H_2 capacity/tanker[2]



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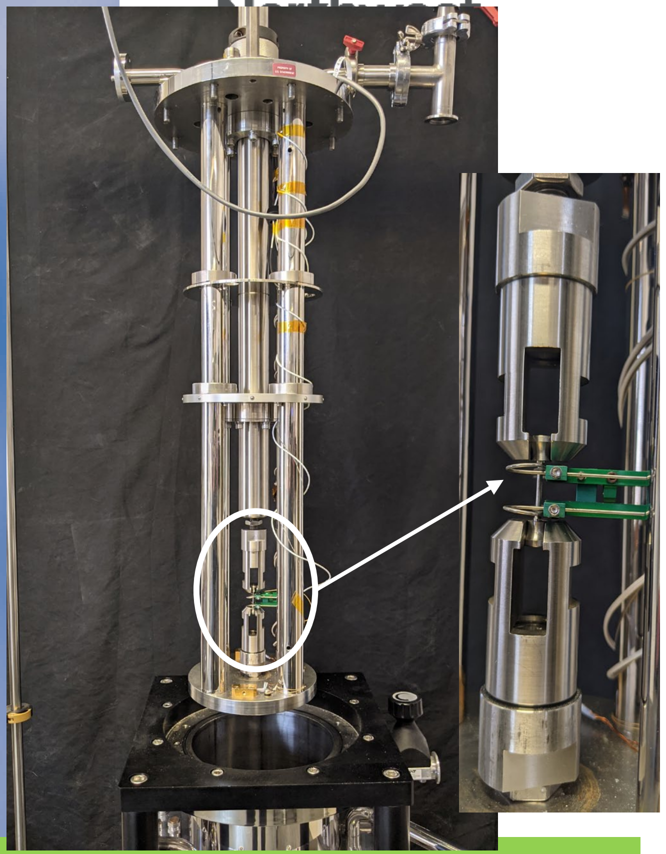
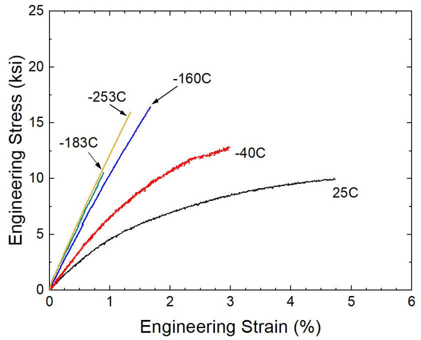
LH2

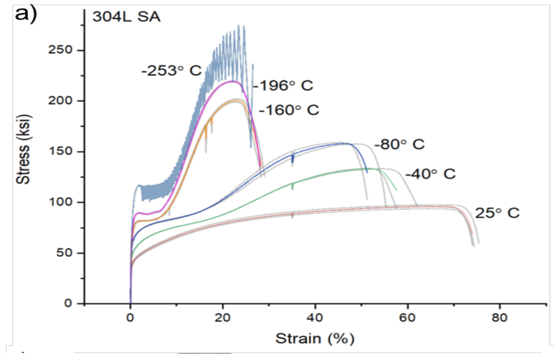
4,300 kg H_2 capacity[3]

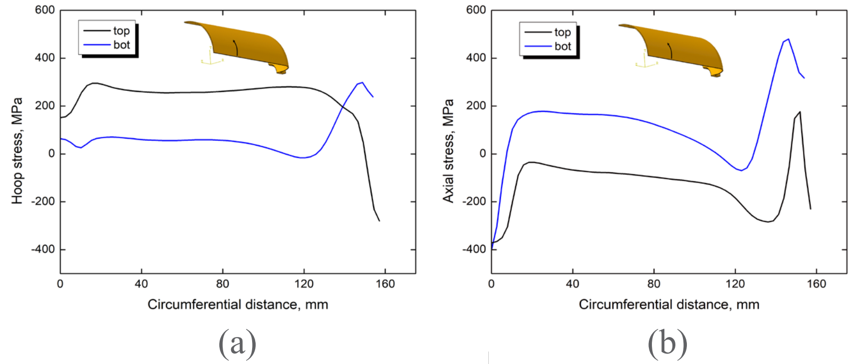
1. Adapted from Petitpas et al. DOE FCTO AMR June 6th 2017.
2. https://www.catecgases.com/
3. http://www.airproducts.com/~/media/downloads/h/hydrogen2/data-sheets/en-smartfuel-hydrogen-supply-options.pdf

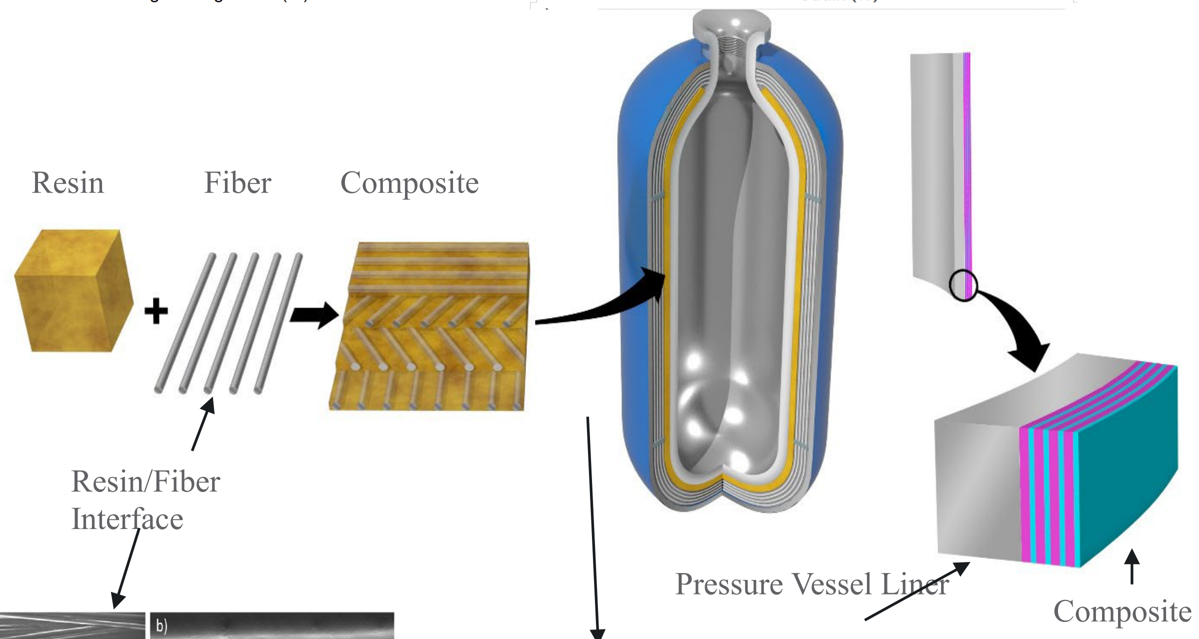
Investigating Cryogenic and Hydrogen Effects on Materials for Liquid and Cryo-Compressed Storage

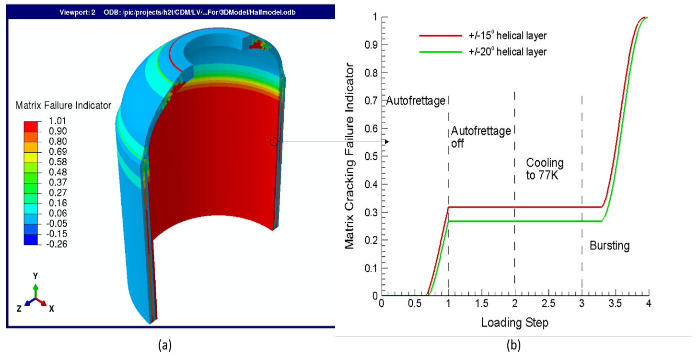


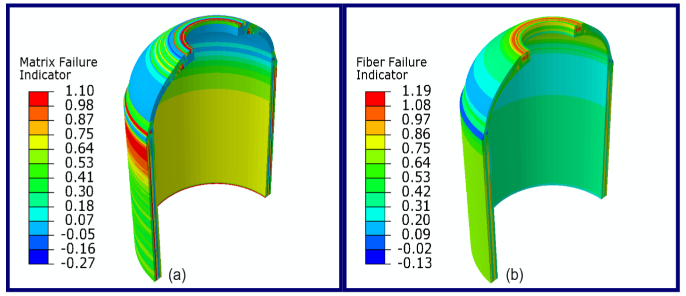




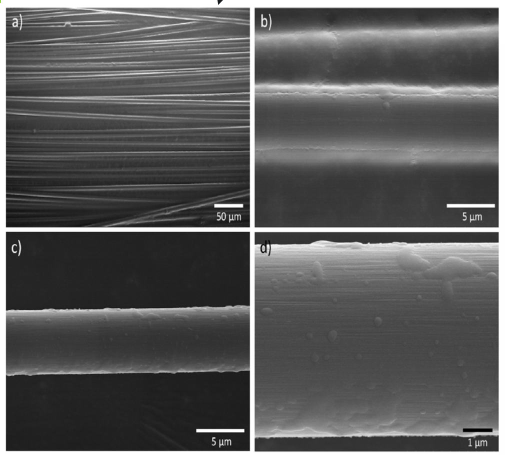


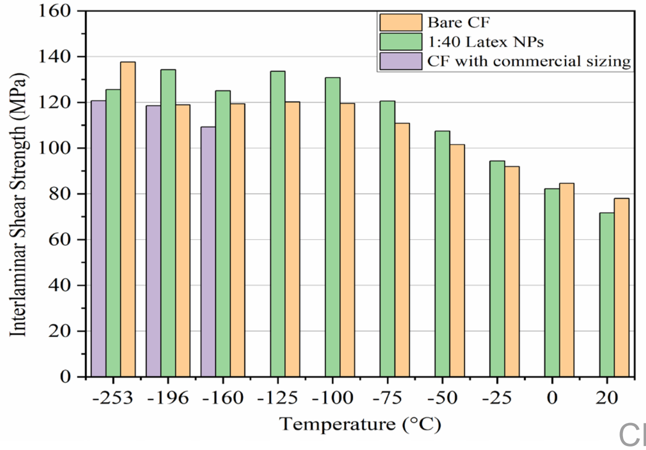


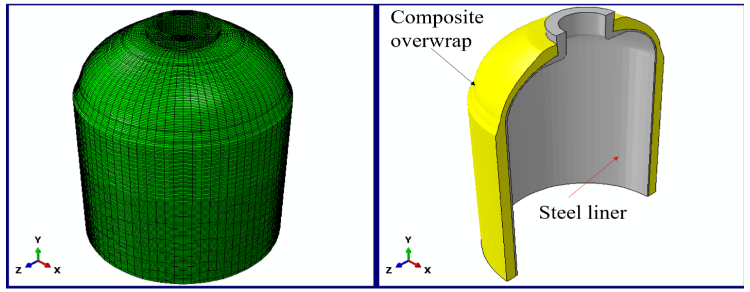




- Increased interlaminar shear strength performance
- Matrix and composite failure indicator models developed with 20K data
- Observed hydrogen effects on metals and welds at 20K

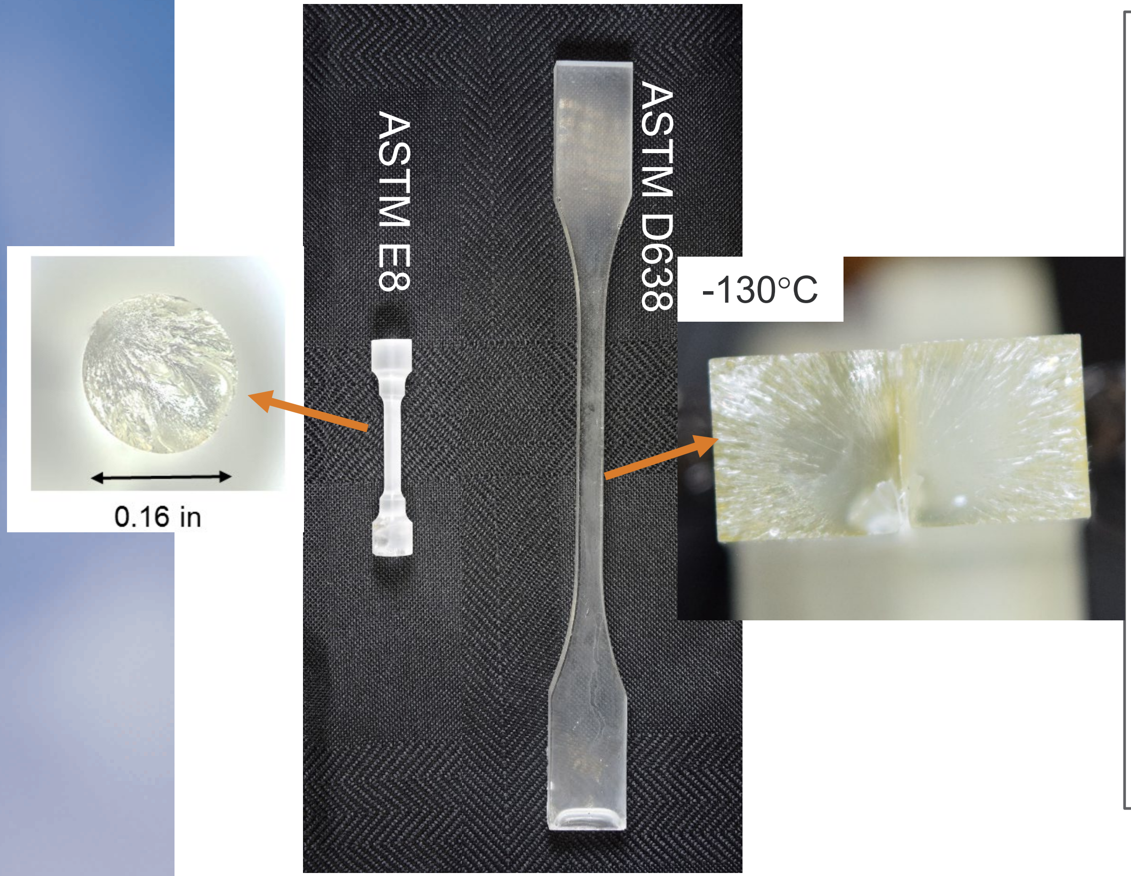






Resins for Cryogenic Service

- Low temperature and toughened resin systems provide for cryogenic composite systems for lightweighting
- Low coefficients of thermal expansion (CTE) provide reduced composite stress during thermal cycling
- Still meets processing property requirements

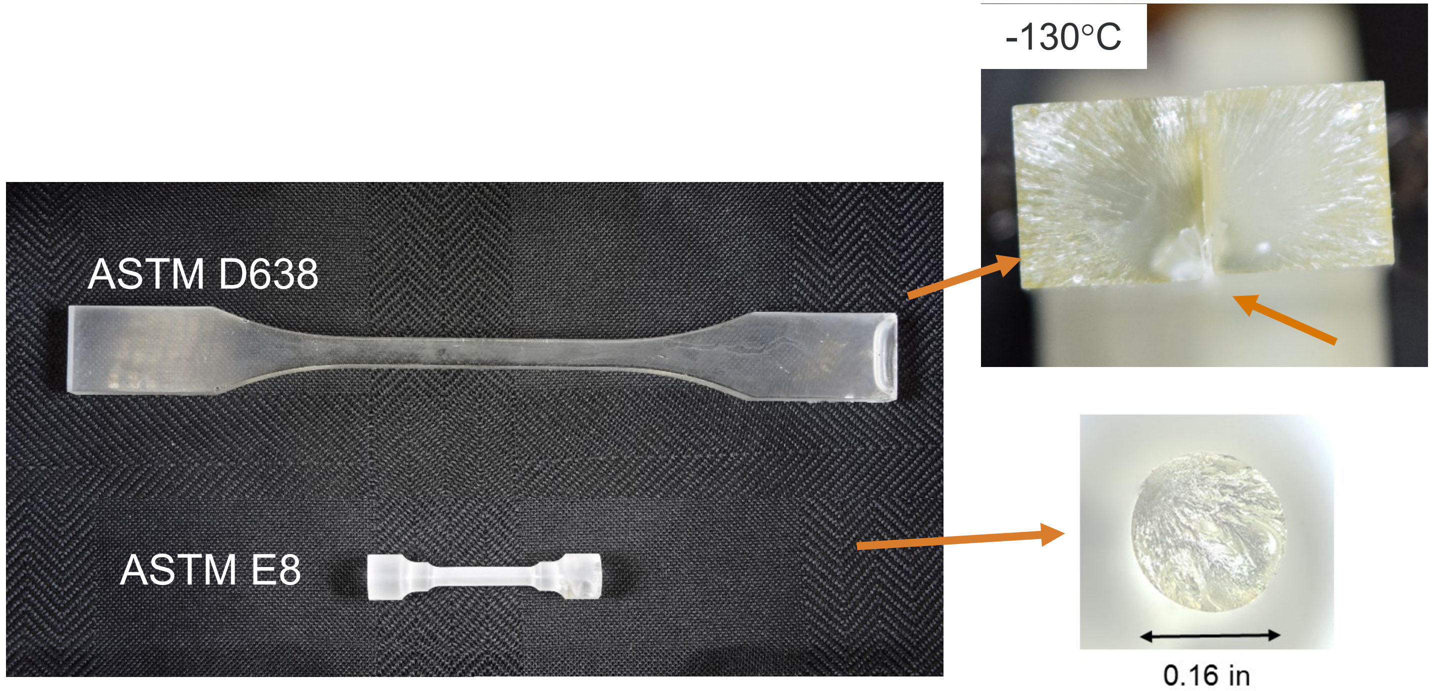


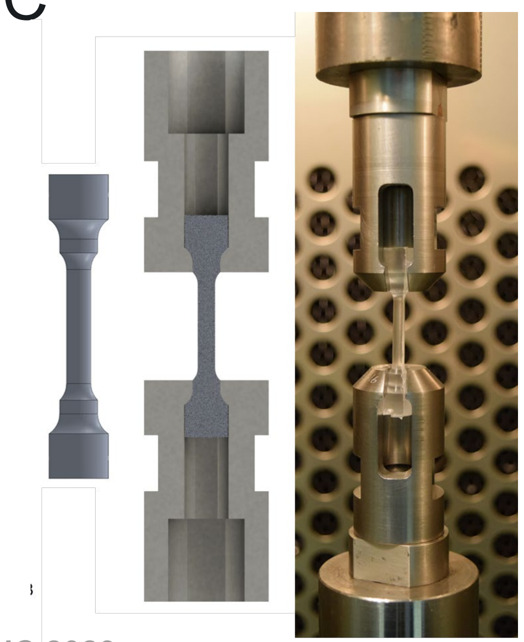
Challenges

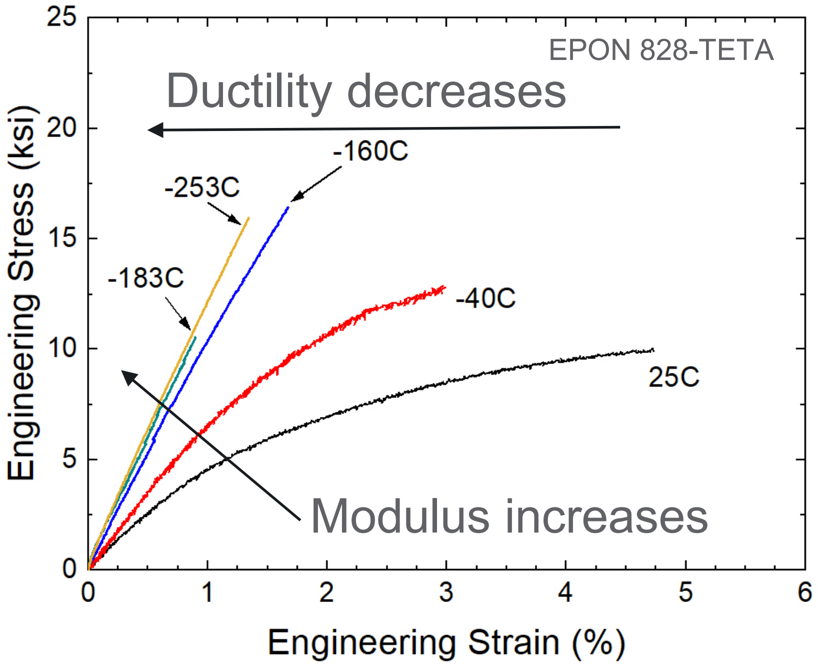
- Critical gap in understanding lower glass transition temperature impacts ambient to higher temperature composite performance
- Outgassing into vacuum space
  - Epoxy materials have specific outgassing signatures which are easily identified and quantitated. This technique is useful to optimize pre-seal bake out and to identify thermal stress by-products
  - Moisture and CO_2 are generally the main compounds outgassed from epoxy materials mainly because of under curing or over curing problems
  - GC/MS analysis will detect organic constituent differences between properly and improperly cured or mixed samples, typically silicones

Resin Mechanical Testing

- ASTM D638
  - Square cross-section
  - Defect sensitivity at corners
- ASTM E8
  - Circular cross-section
  - Reduced specimen size
  - ~40% increase in strength at -130˚C
- Cryo results
  - Increase in modulus at lower temperatures
  - Defect sensitive reduces strength

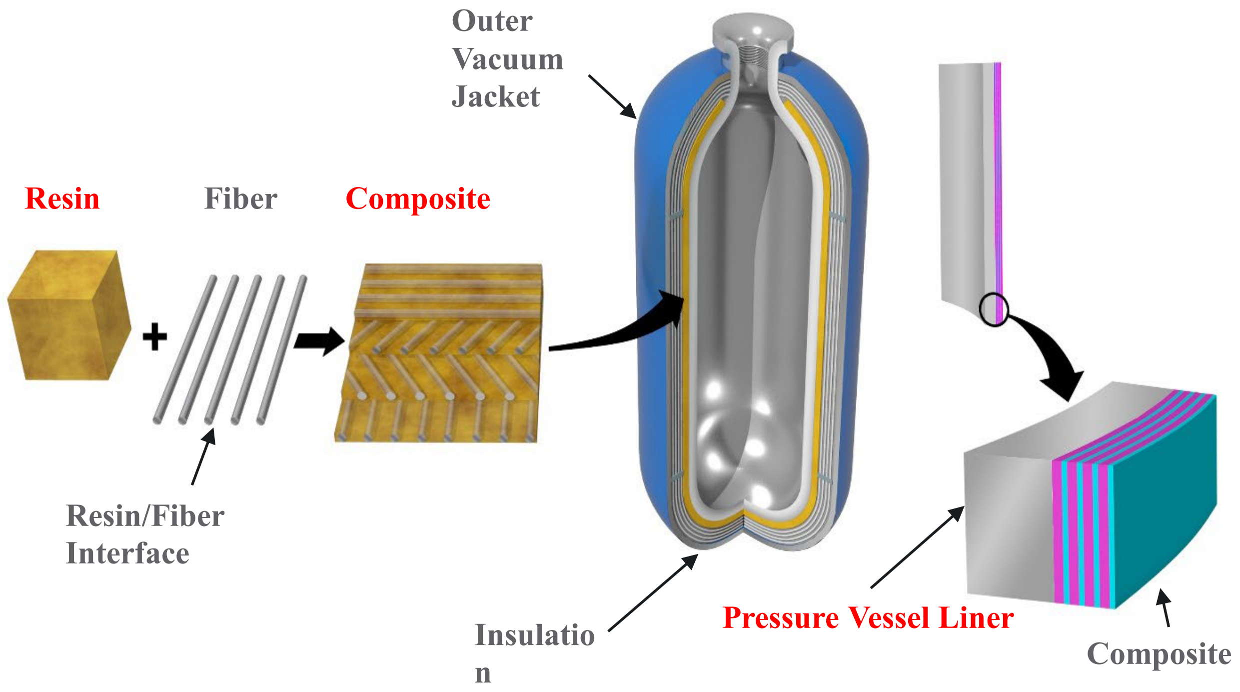






Composites for Cryogenic Service

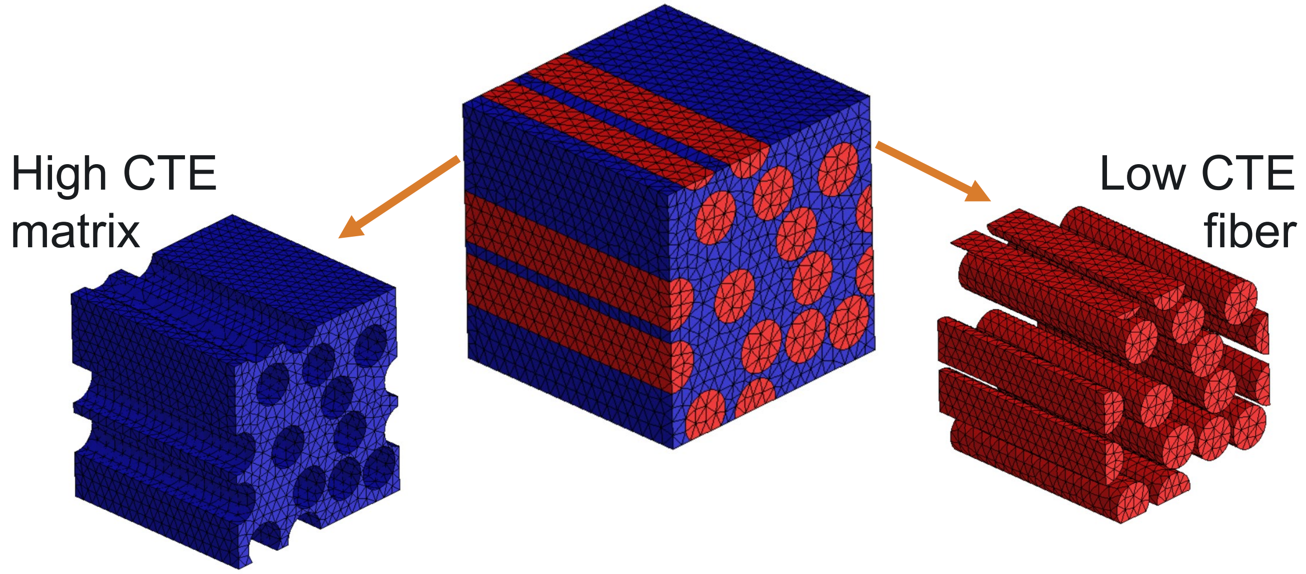
- Composites provide excellent weight reduction and strength
  - Common fibers are carbon and glass fibers
- Technologies proven in aerospace and space applications
- Tailored system designs with resin, fiber, and storage vessel performance



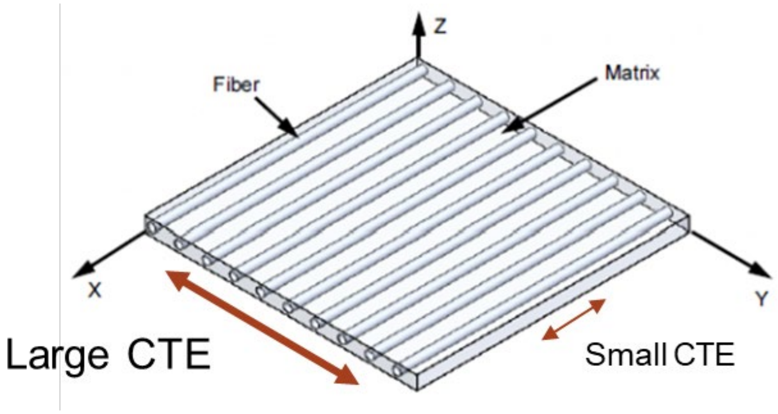
Challenges

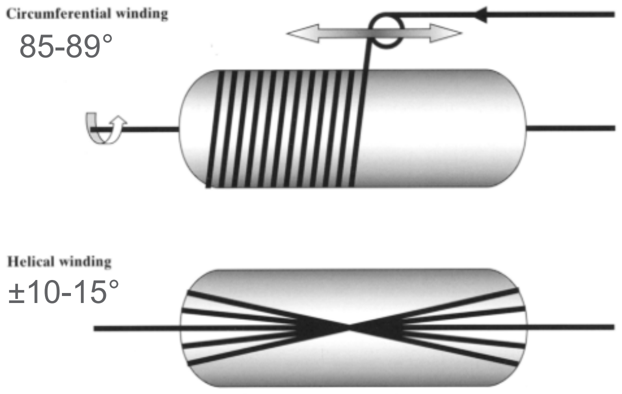
- Thermal cycling of composites
  - Coefficient of thermal expansion differences between resin and fiber
  - Matrix microcracking coalesces into macro cracks
  - High strain at the fiber/resin interface produces interfacial debonding
- Combined pressure cycling for fatigue endurance with thermal effects

Composite overwrap

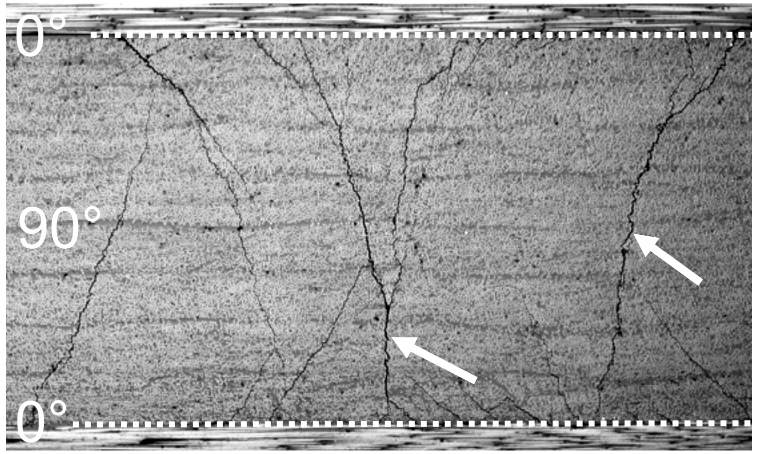


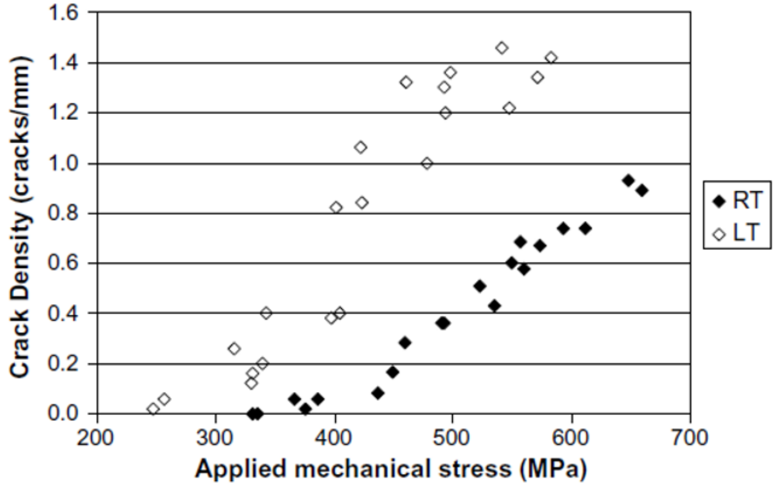
- Matrix thermal embrittlement
  - Defect sensitive
- Fiber-matrix thermal expansion mismatch
  - Fiber-matrix bond
- Non-isotropic layup
  - Hoop windings at 85-89°
  - Helical windings at 10-15°
- Matrix cracking
  - Thermal-induced
  - Pressure-induced
  - Fatigue-induced





Biron, *Thermosets and Composites* 2004

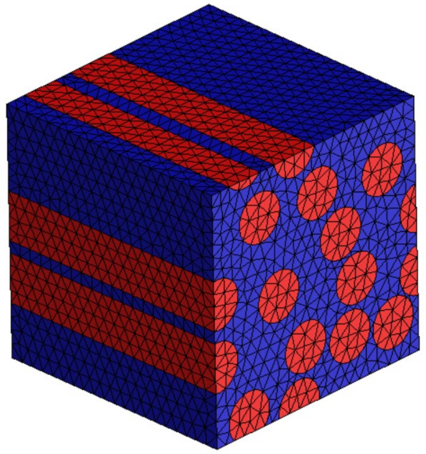


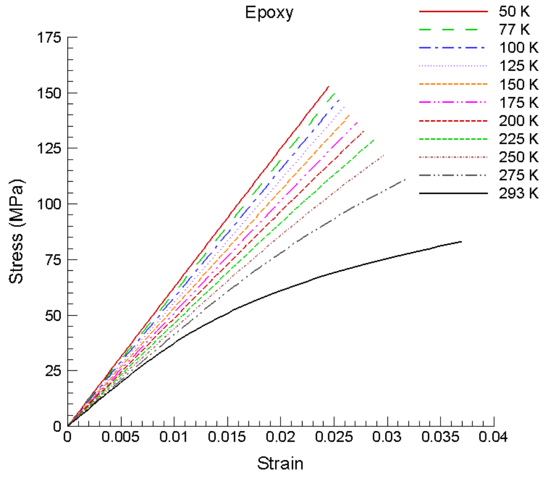


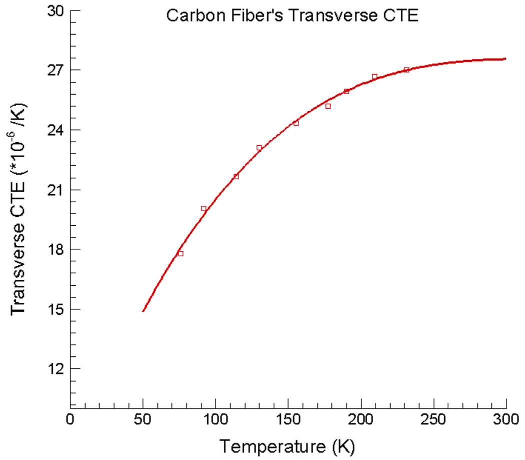
Lundmark and Varna, Engineering Fracture Mechanics 75 (2008) 2631–2641

Materials Modeling to Storage Vessel Approach

Temperature-dependent composite







Temperature-dependent liner

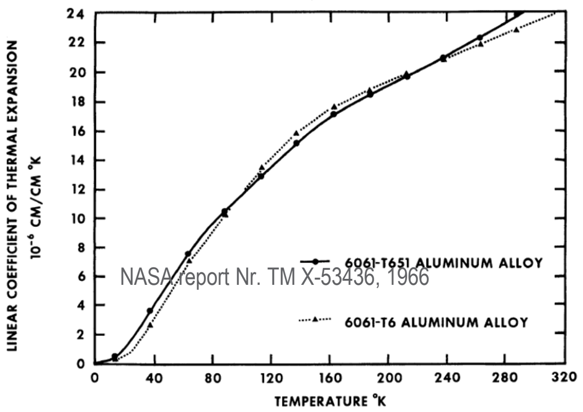
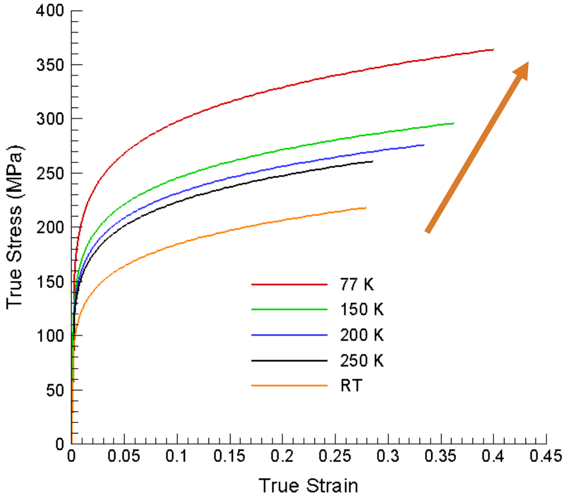
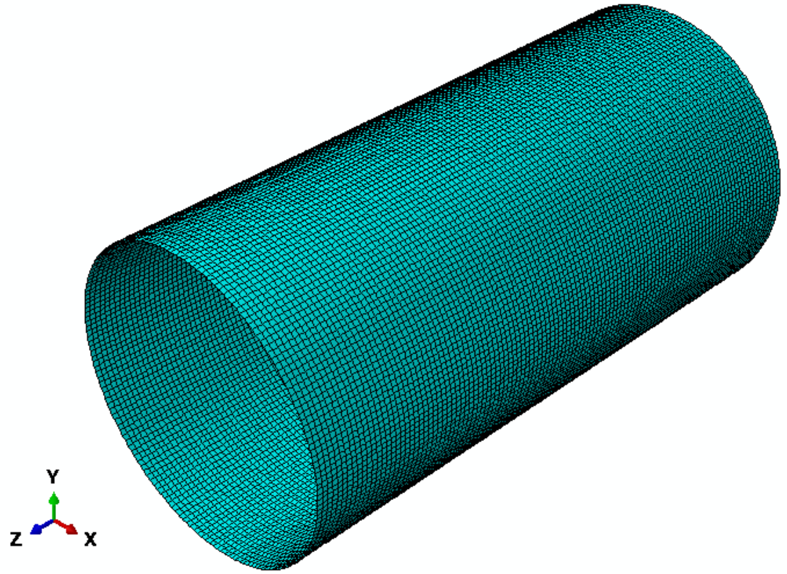


FIGURE 12. - LINEAR COEFFICIENT OF THERMAL EXPANSION, 6061 - T651 AND 6061 - T6 ALUMINUM ALLOY

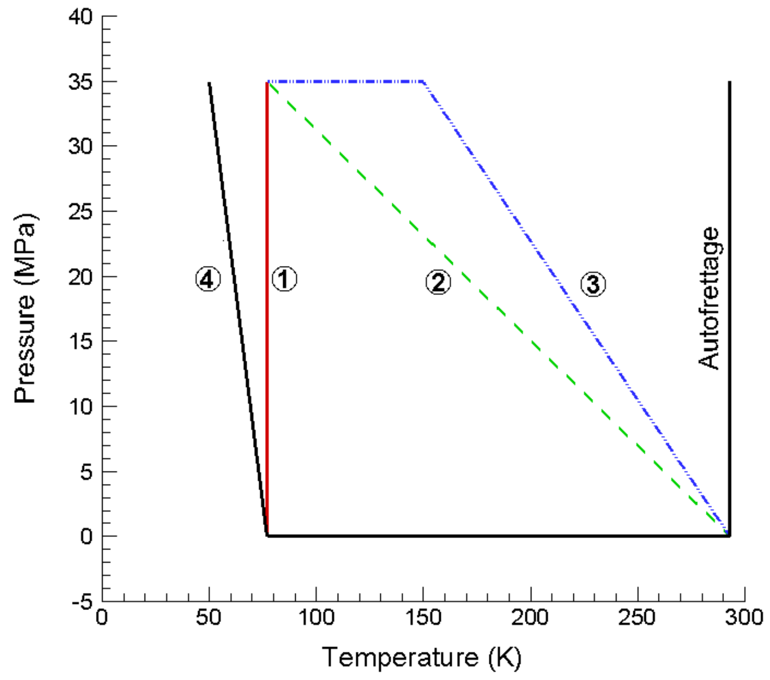


Tank

- Layup: Al liner/90˚/+10˚/-10˚
- Fiber volume fraction: 0.6
- Dome simulated with distributed load



Modeling: Loading scenarios



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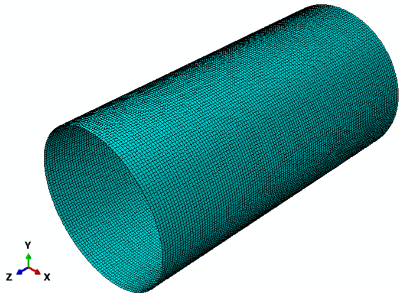
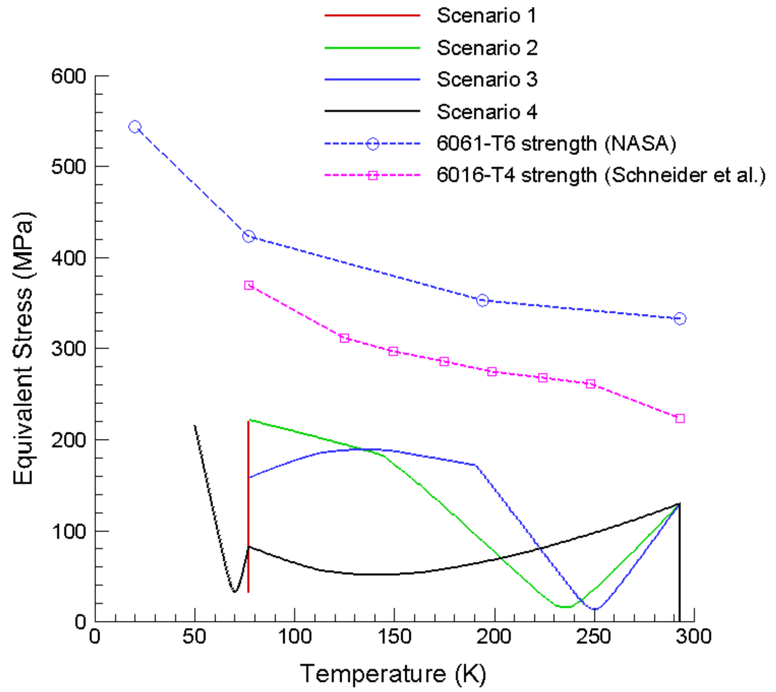
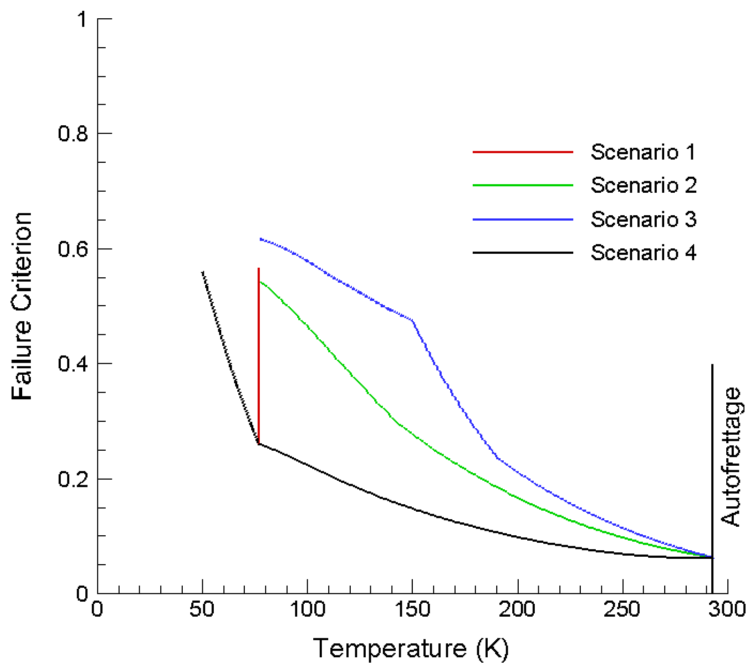


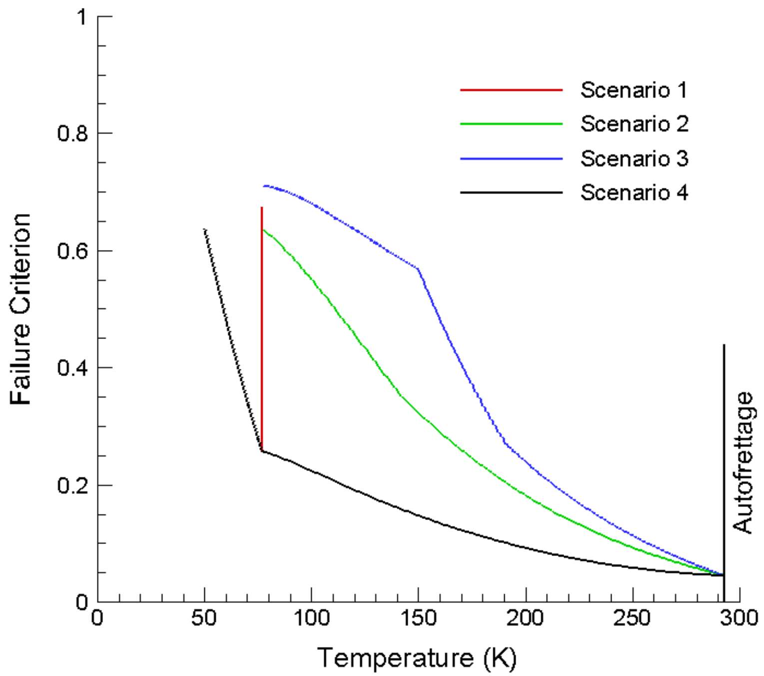
Nguyen, et al International Journal of Hydrogen Energy 45 (46), 24883-24894



Al liner



90 Hoop layer



10 Helical layer

Pressure Vessel Liner Issues

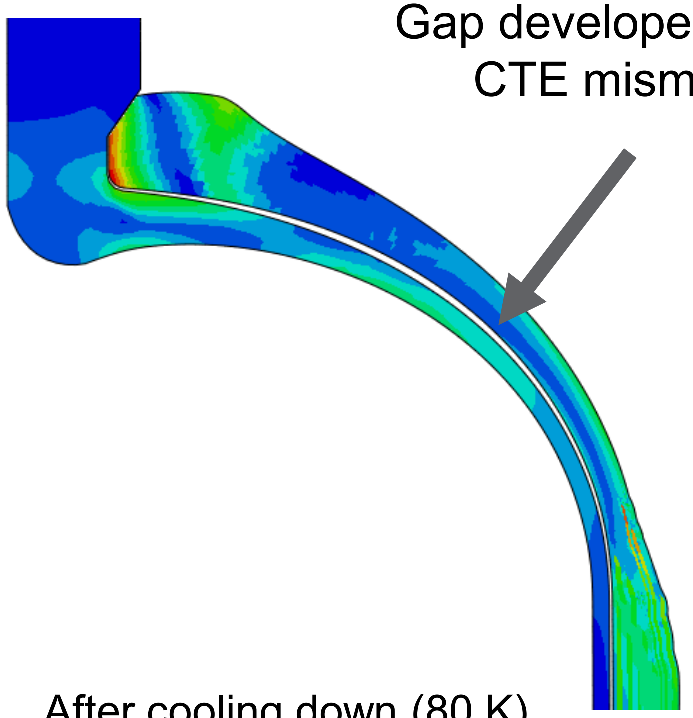
<u>Metallic material H2 compatibility</u>

- Welding liner materials
  - Weld quality
  - Weldability of materials
  - Fatigue endurance limits of welds
  - Cryogenic performance
- Coefficient of thermal expansion mismatch with metallic liner and composite
  - Compressive cyclic fatigue
  - Added mass to compensate for fatigue endurance limits
- Need material data for pressure vessel designs for applicable temperatures:
  - Yield strength
  - Ultimate strength
  - Fatigue strength
  - Ductility limits
  - Creep
  - Thermal expansion coefficients

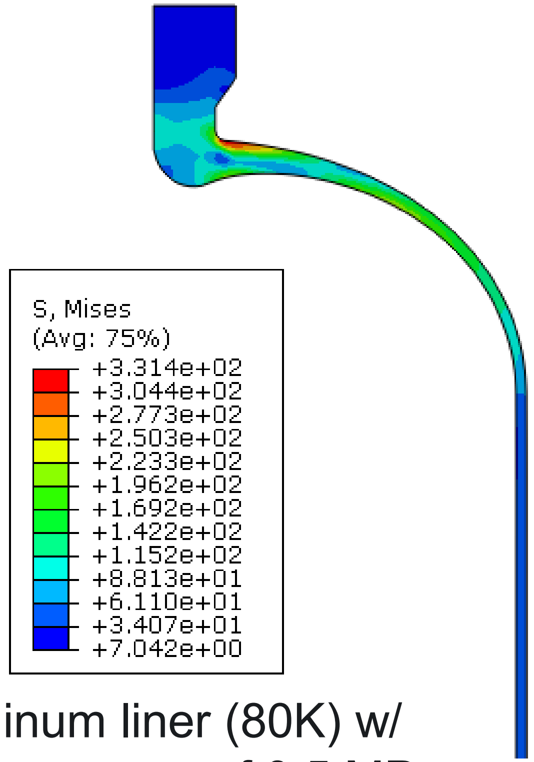
Modeling: Full tank FEA

- Illuminates issues associated with dome section and boss
  - Liner buckling during autofrettage
  - Gap formation during cooling

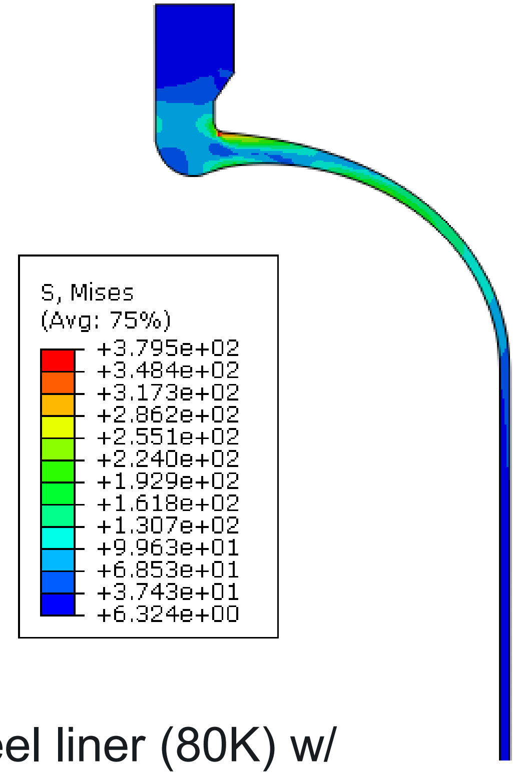
Gap developed due to CTE mismatch



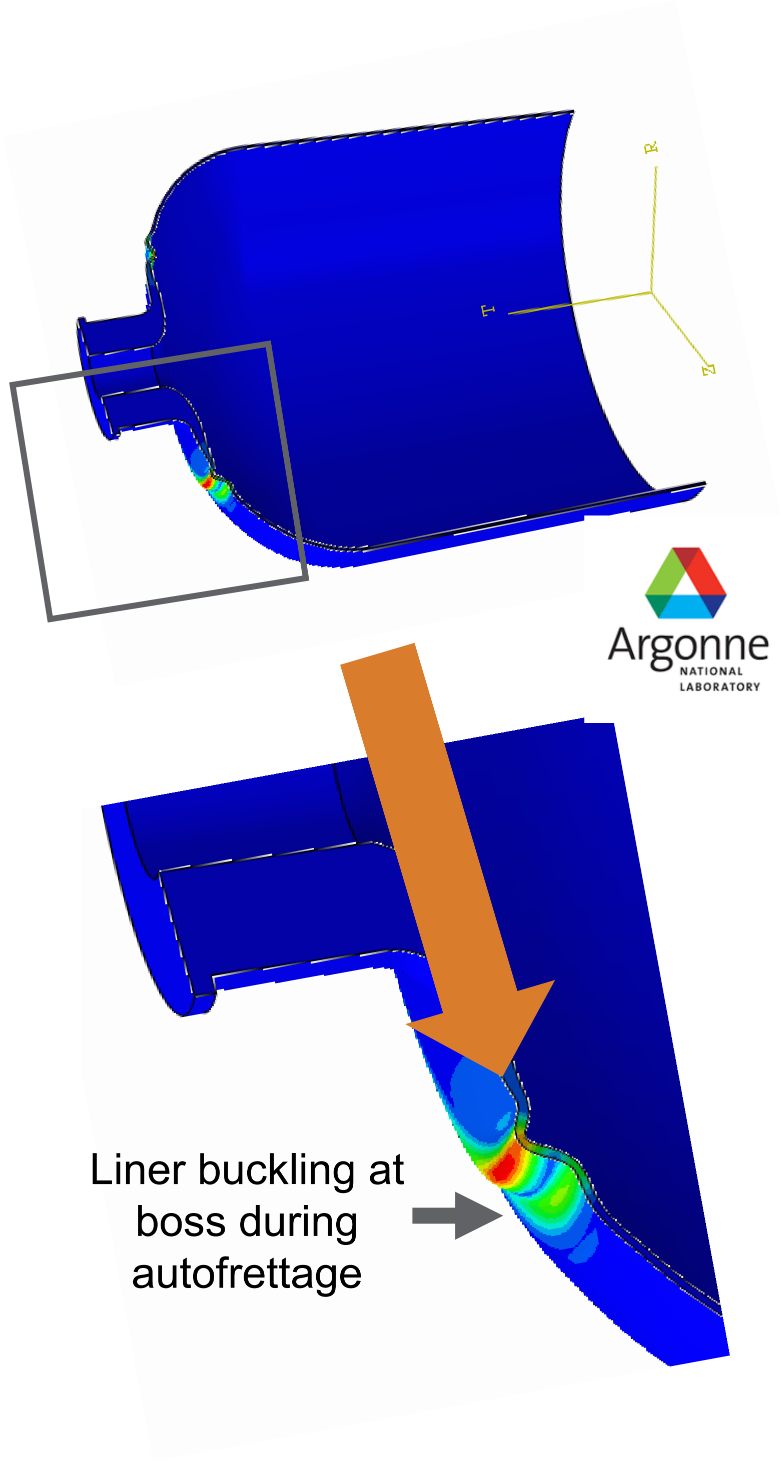
After cooling down (80 K)



Aluminum liner (80K) w/ empty pressure of 0.5 MPa



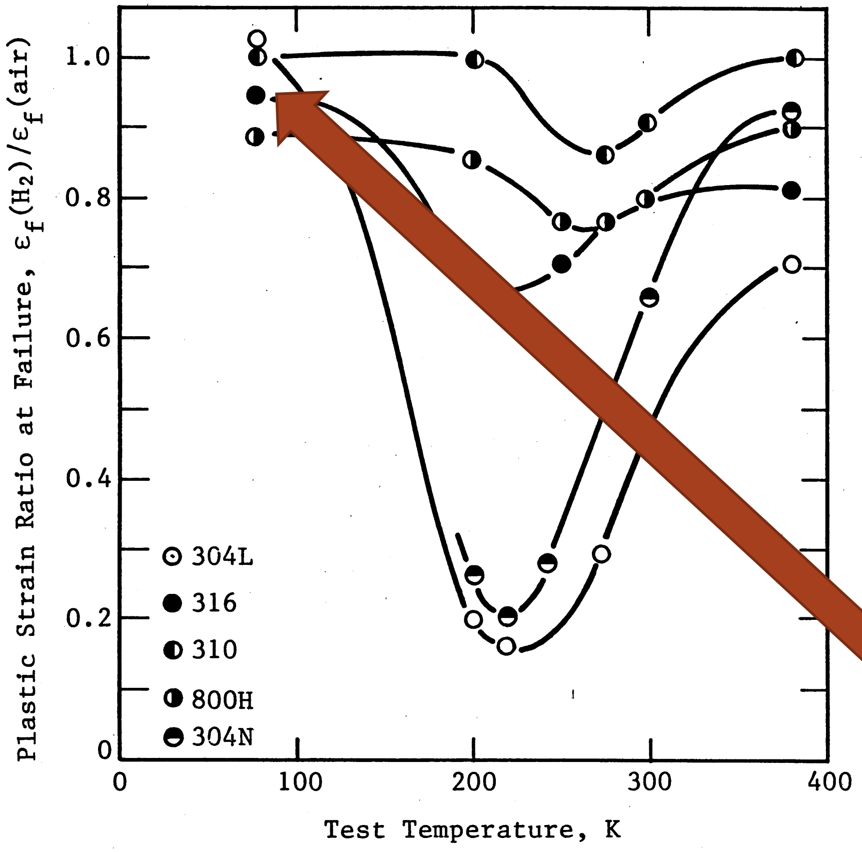
Steel liner (80K) w/ empty pressure of 0.5 MPa



Liner buckling at boss during autofrettage

Metals for cryogenic service

- Austenitic stainless steels are baseline for LH2 service: 304L and 316L
  - Stable austenitic stainless steels may offer improved performance: Nitronic 40 (XM-11) and Nitronic 50 (XM-19)
- Aluminum alloys are not degraded at cryogenic temperature
  - Weldable alloy for space shuttle LH2 tanks: AA2219



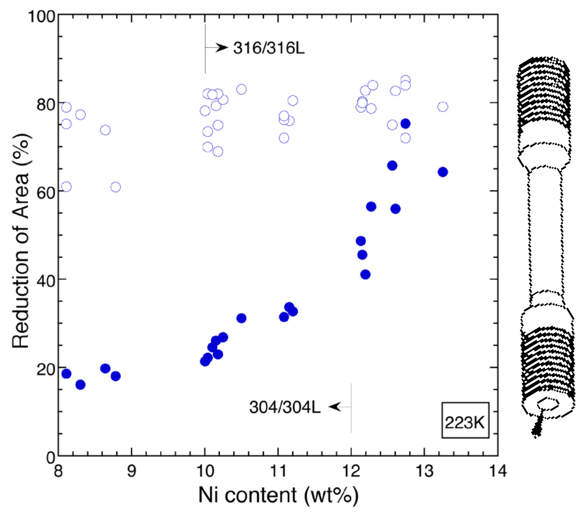
Challenges

- Welds are suspect in applications that require welded-construction with high fatigue stresses, such as cryo-compressed containers
- Aluminum alloys tend to display inferior fatigue properties compared to steels
- Appropriate test methodology for cryogenic hydrogen is not known
  - For example, time scales for hydrogen uptake and transport at low temperature may determine the manifestation of hydrogen effects
  - Testing artifact at low temperature or representative of long term behavior?

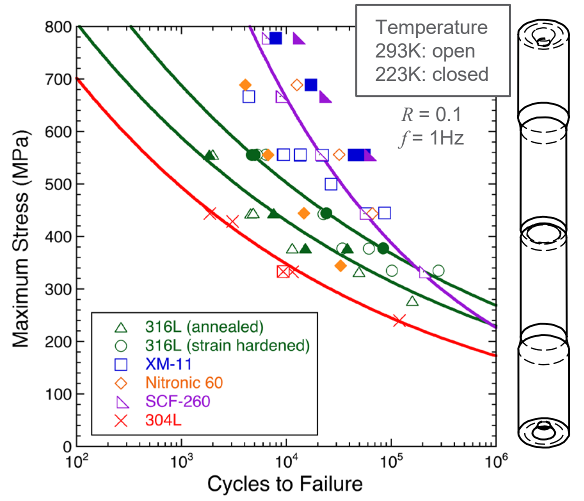
Approach to understanding materials behavior in cryogenic hydrogen environments

- Establish baseline behavior of low-cost candidate materials in cryogenic hydrogen environments (temperature: 30 to 300K) relative to accepted performance metrics for ambient service and baseline materials
  - Use H-precharging to overcome kinetics of hydrogen uptake†
  - Evaluate high-performance welds and base materials of austenitic stainless steel: 304L
  - Evaluate high-performance welds and base materials of austenitic stainless steel: Nitronic 50 (XM-19)

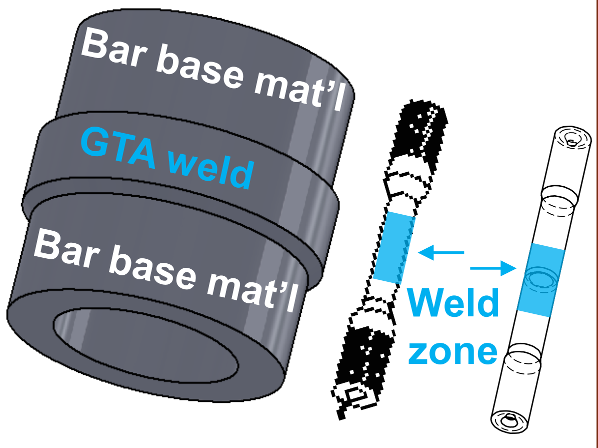
Slow strain rate tension



Notched fatigue life



Welds

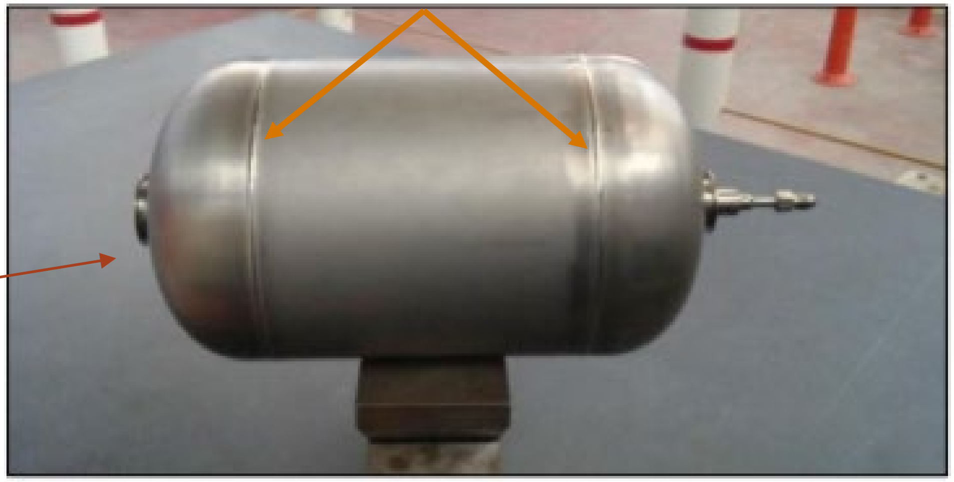


†must consider effect of H-supersaturation on strength properties and kinetics of hydrogen transport at low temperature

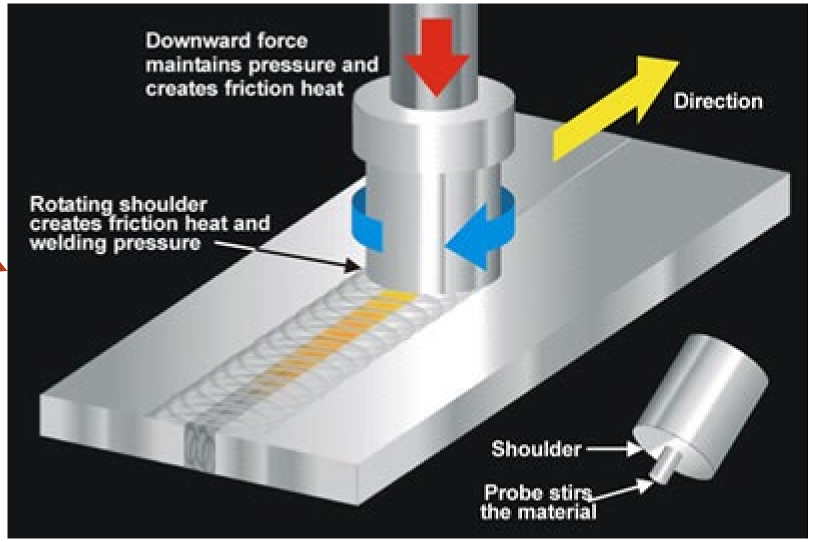
Storage Vessel Metal Liners

- Materials
  - 304, 316, Nitronic 50 steels
  - Aluminum 2219
- Welded zones
  - Traditional welding
  - Friction stir welding
- Test temperatures
  - 113 K (-160°C) - LNG
  - 77 K (-196°C) - LN_2
  - 20 K (-253°C) - LH_2
- Temperature effects
  - σ_y increase
- Hydrogen embrittlement
  - ε_f decrease

Welded dome-ends



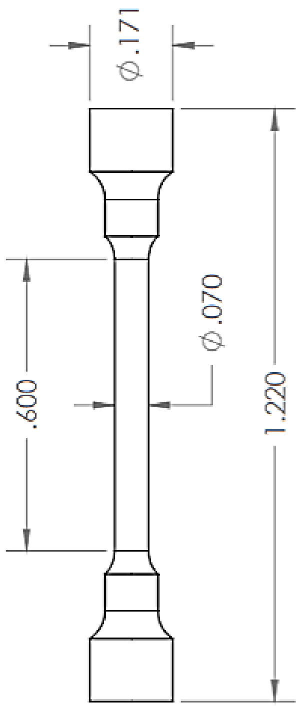
Akin et al, "Design, Analysis and Manufacture of Composite Overwrapped Xenon Propellant Tank" 2017



Friction Stir Welding - *ASME Columbia Basin*

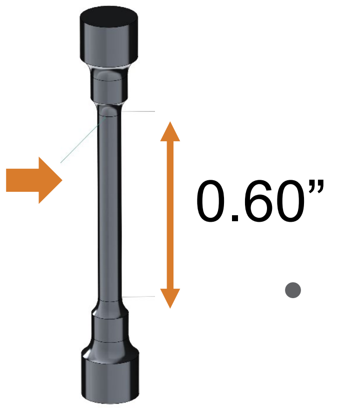
Testing conditions

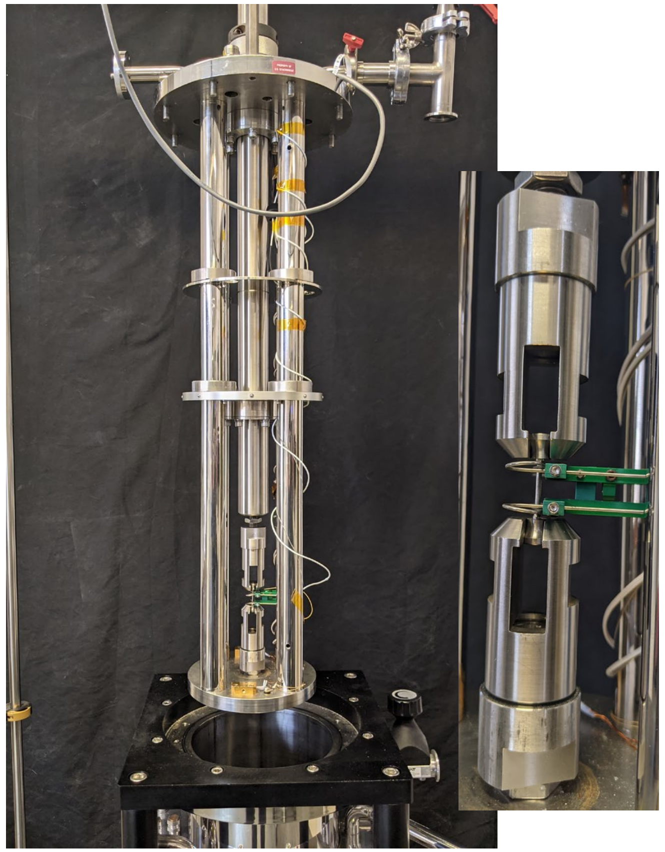
Cooling Method		Temperature °C	Temperature K	Reference
Environmental chamber	LN_2-cooled	25	298	Room
		-40	233	Tank Fill
		-80	193	CO_2
Cryostat	LN_2-cooled	-160	113	LNG
		-196	77	LN_2
	LHe-cooled	-253	20	LHe



Hydrogen pre-charged

- H_2 gas at 138 MPa, 573 K, 10 days
- 140 wt ppm (saturated)



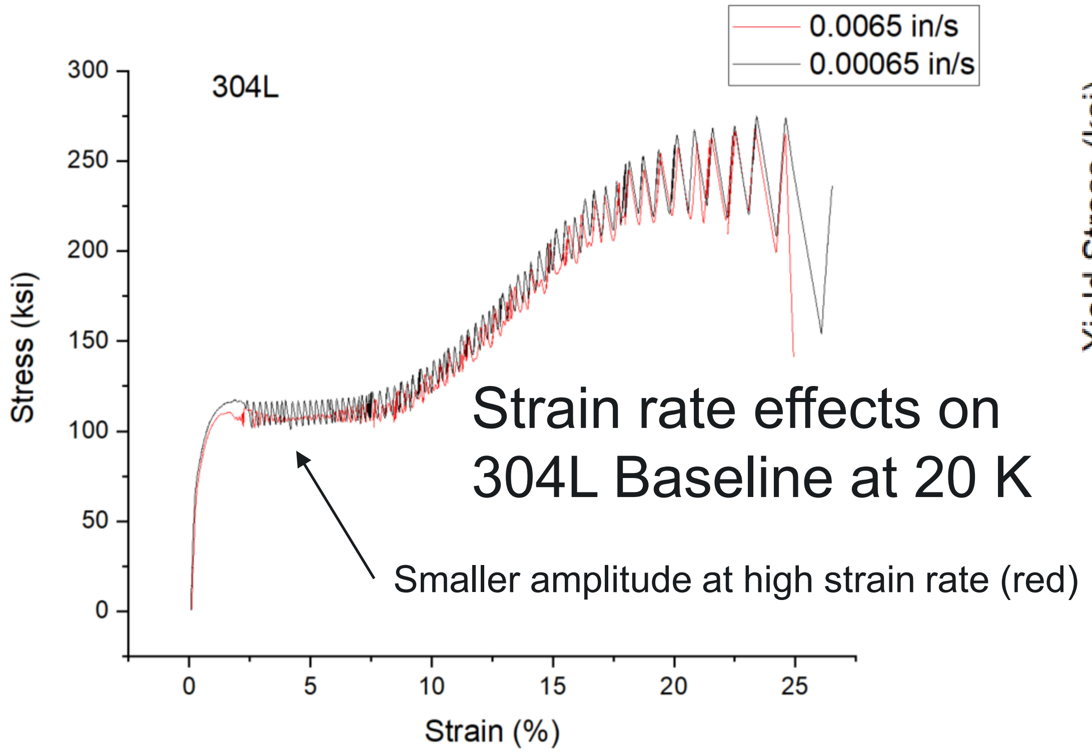


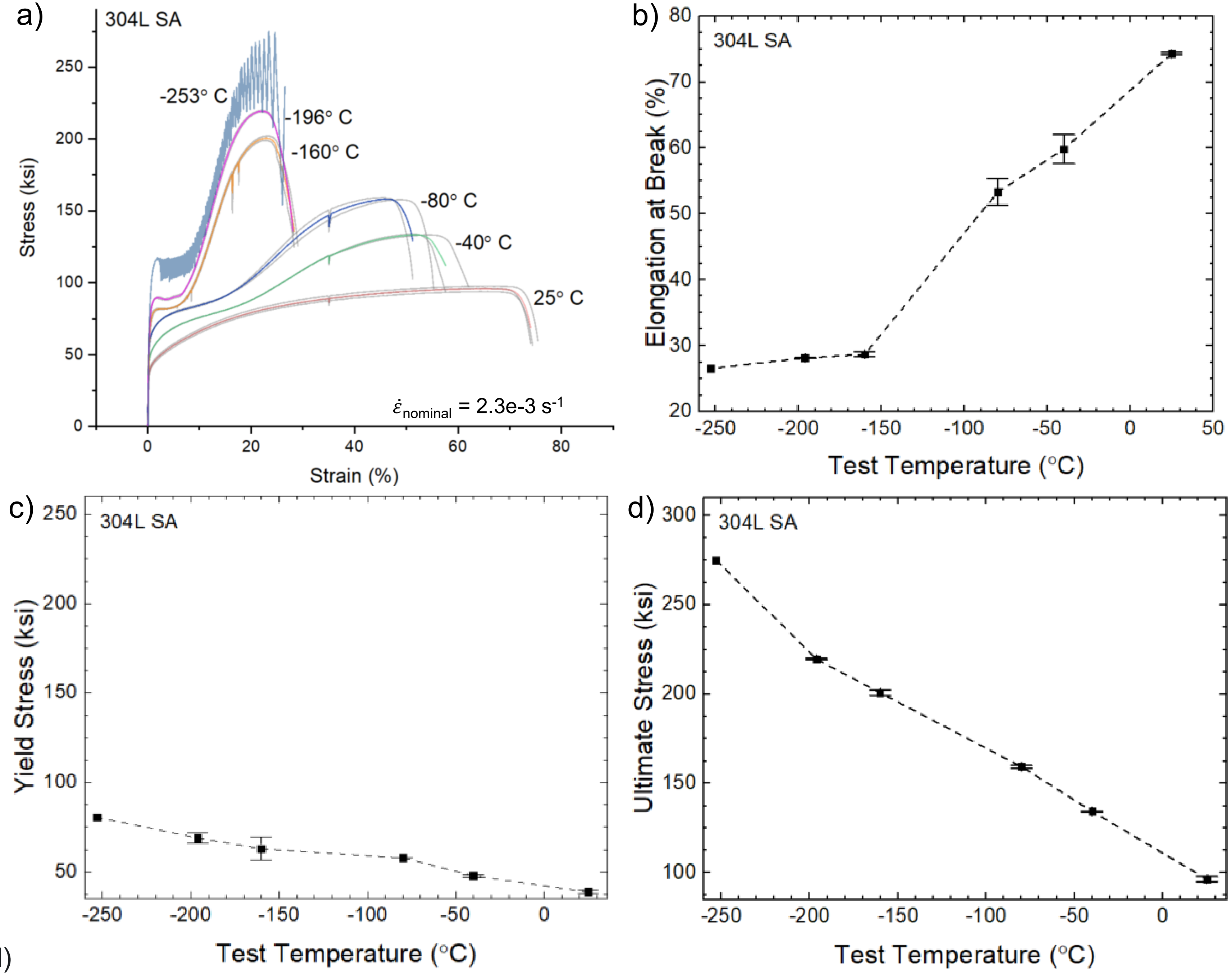
- Machine rate: 0.039 in/min
  - Nominal strain rate: 2.3e-3 s^{-1}

Composition of metals used in this study																
Designation	Fe	Cr	Ni	Mn	Mo	Si	C	N	S	P	Cu	Co	Sn	V	Cb	B
304L	Bal	18.17	8.50	1.38	0.320	0.21	0.017	0.077	0.024	0.034	0.38	0.26	-	-	-	-
N50 (XM-19)	Bal	21.36	11.90	4.98	2.12		0.034	0.34	0.002	0.022	0.40	<0.05	0.003	0.15	0.15	0.005

304L Baseline

- Annealed
  - 1050°C 30 min
  - Water quenched
- Apparent influence on serration amplitude at low strain

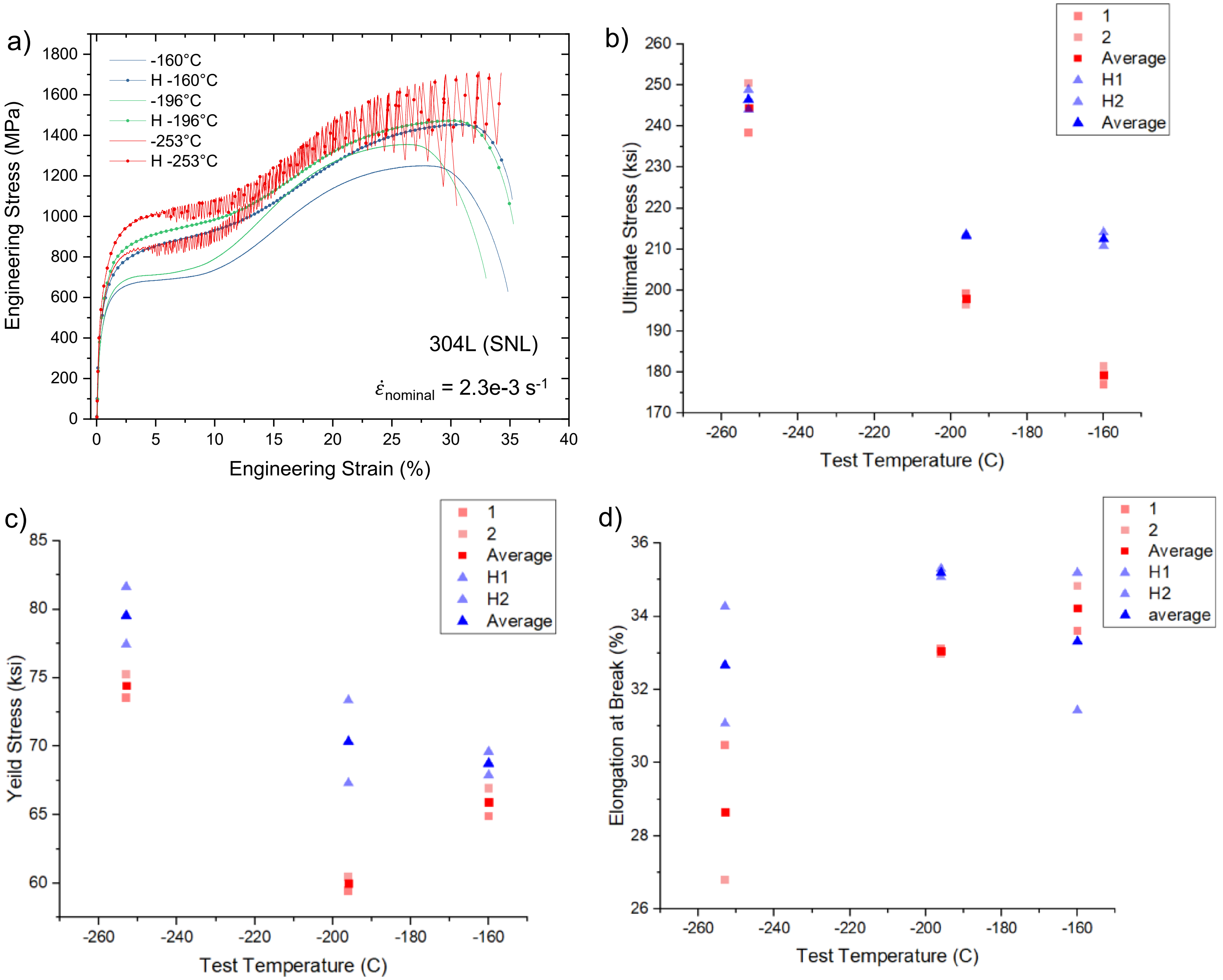




Hydrogen effects on 304L

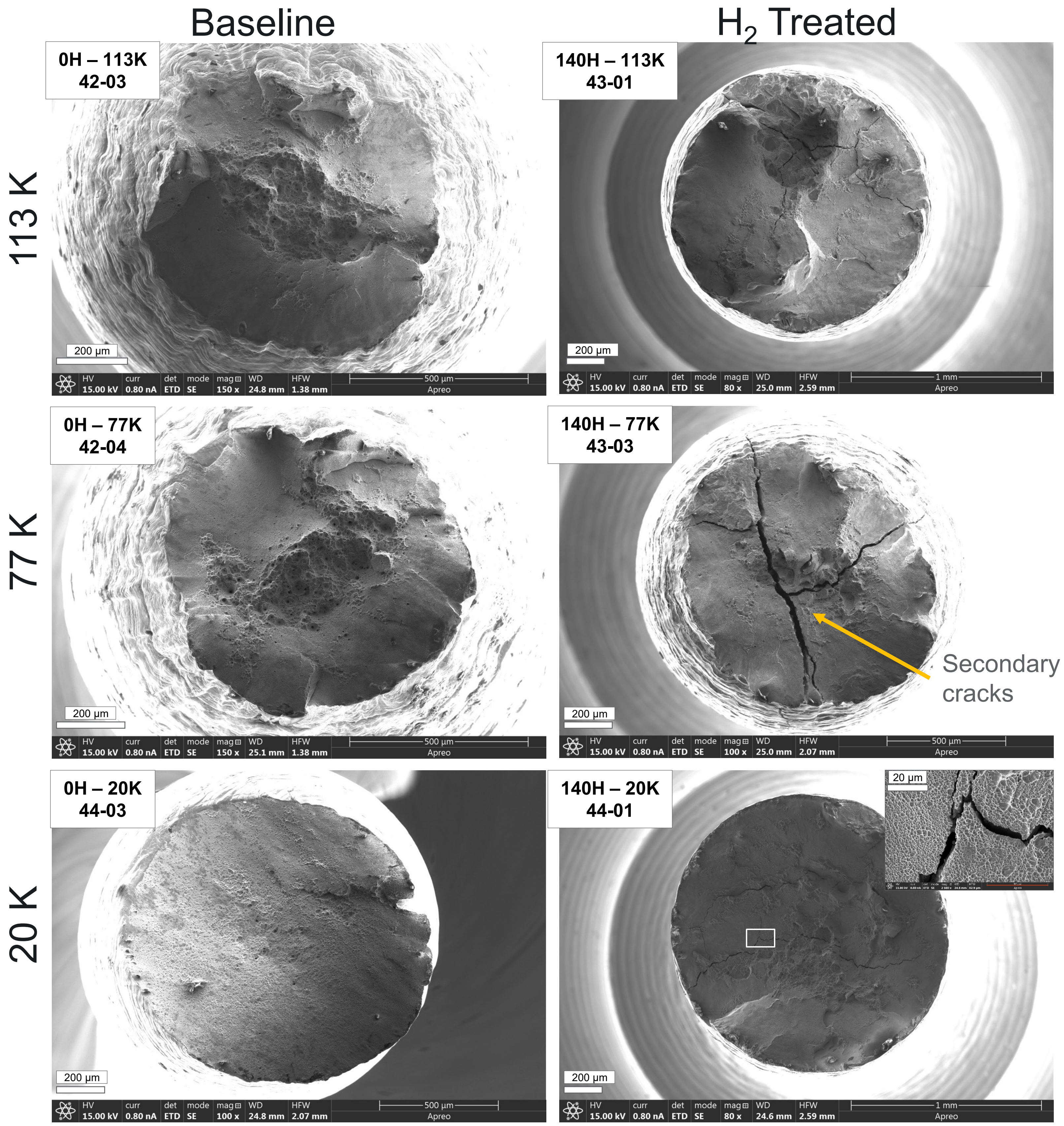
- Charged to 140 wt ppm
- Reduced α’-martensite formation in H-charged 304L
  - Apparent in strain-hardening rate
  - Measured by magnetic methods

Mass% α’-martensite present at fracture surface evaluated by magnetic measurements		
Temperature (K)	**Baseline (0H)**	**Hydrogen-pre-charged (140H)**
113 K (-160°C)	53.1 ±1.7 54.7 ±0.8	42.6 ±0.8 43.8 ±1.6
77 K (-196°C)	54.1 ±1.0 54.4 ±1.2	45.3 ±1.2 45.5 ±0.7
20 K (-253°C)	51.2 ±1.1 53.9 ±2.0	45.2 ±1.1 45.5 ±2.4



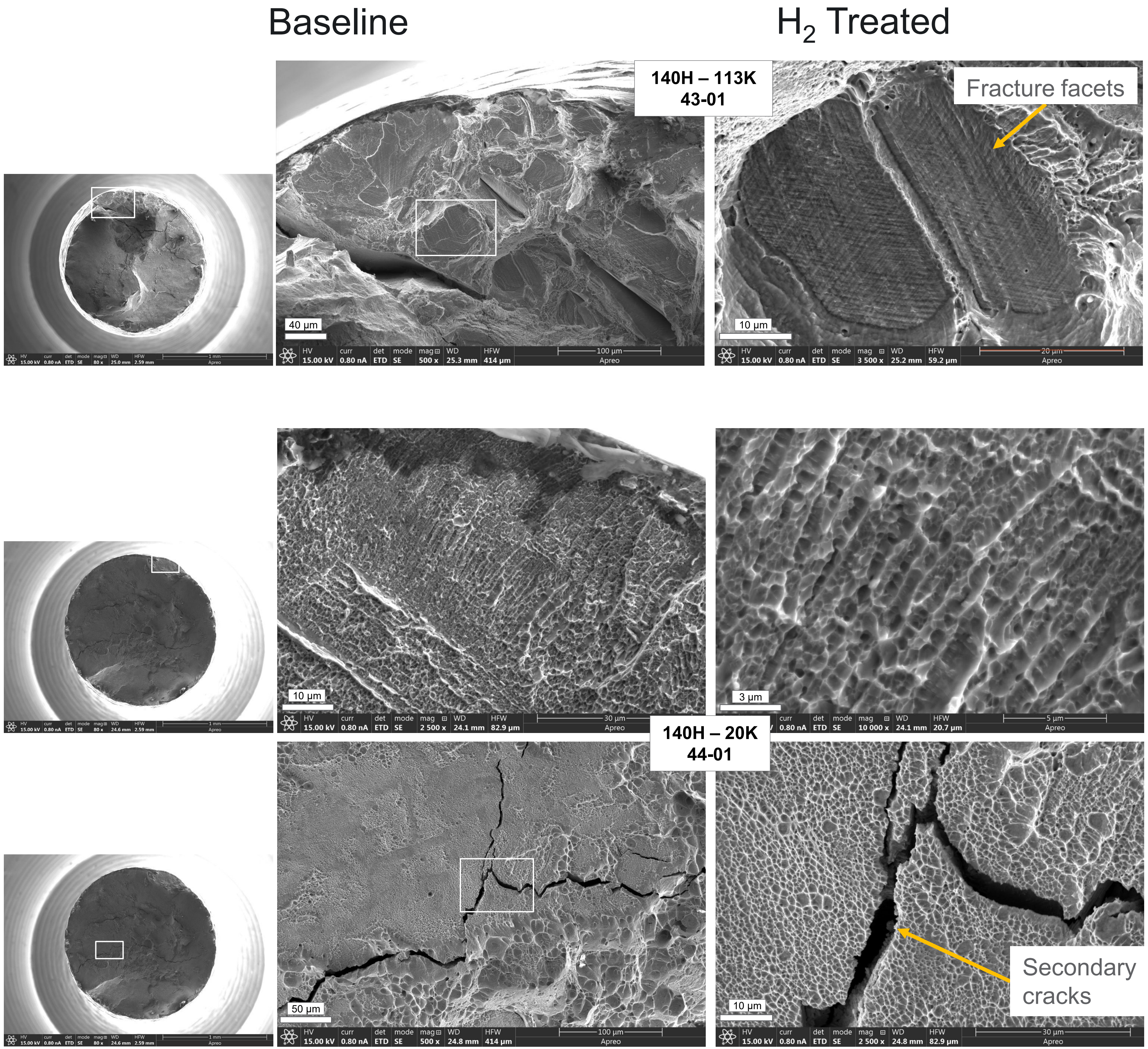
Hydrogen effects on 304L

- Specimens charged to 140 wt ppm
- Secondary cracking observed in fracture surfaces of H-charged specimens



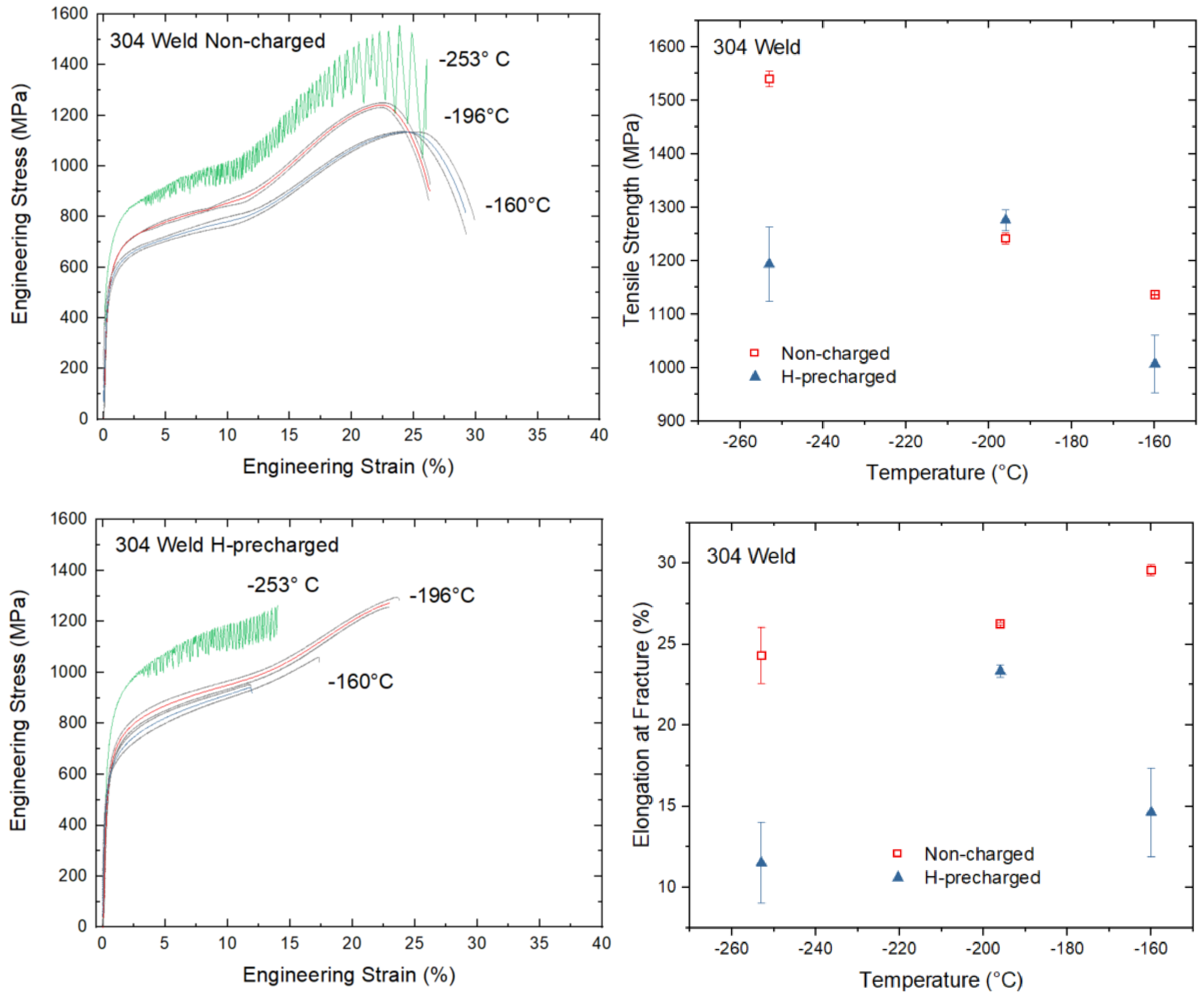
Hydrogen effects on 304L

- Fracture facets observed at 113 K are common observations at high temperature (*e.g.* 223 K)



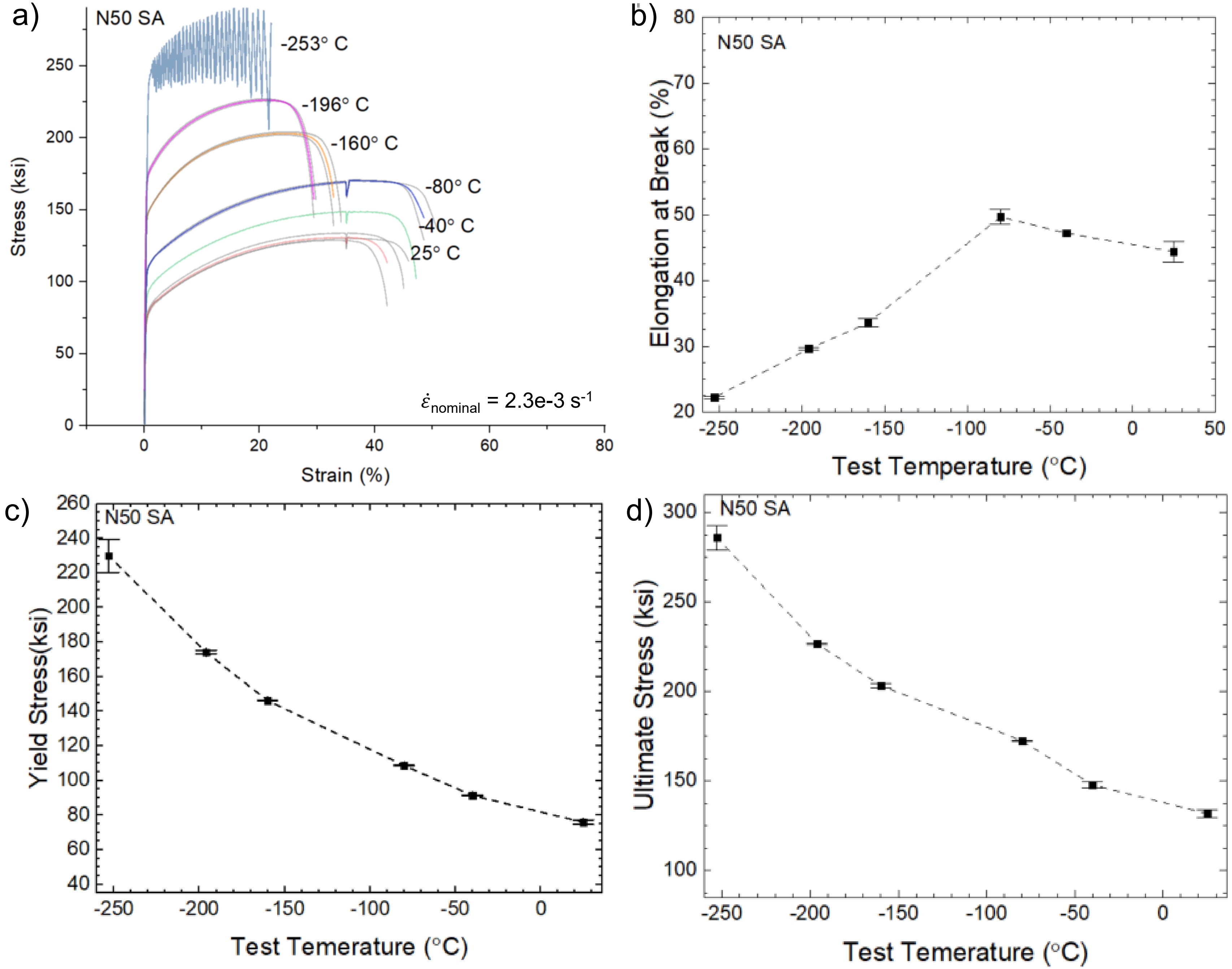
Hydrogen effects on 304L Welds

- Non-charged welded specimens indicate weld ductility down to 20K
- Hydrogen pre-charged welded specimens show hydrogen impacting ductility
- Loss of martensite formation in the hydrogen-charged welded specimens influences the loss in weld ductility



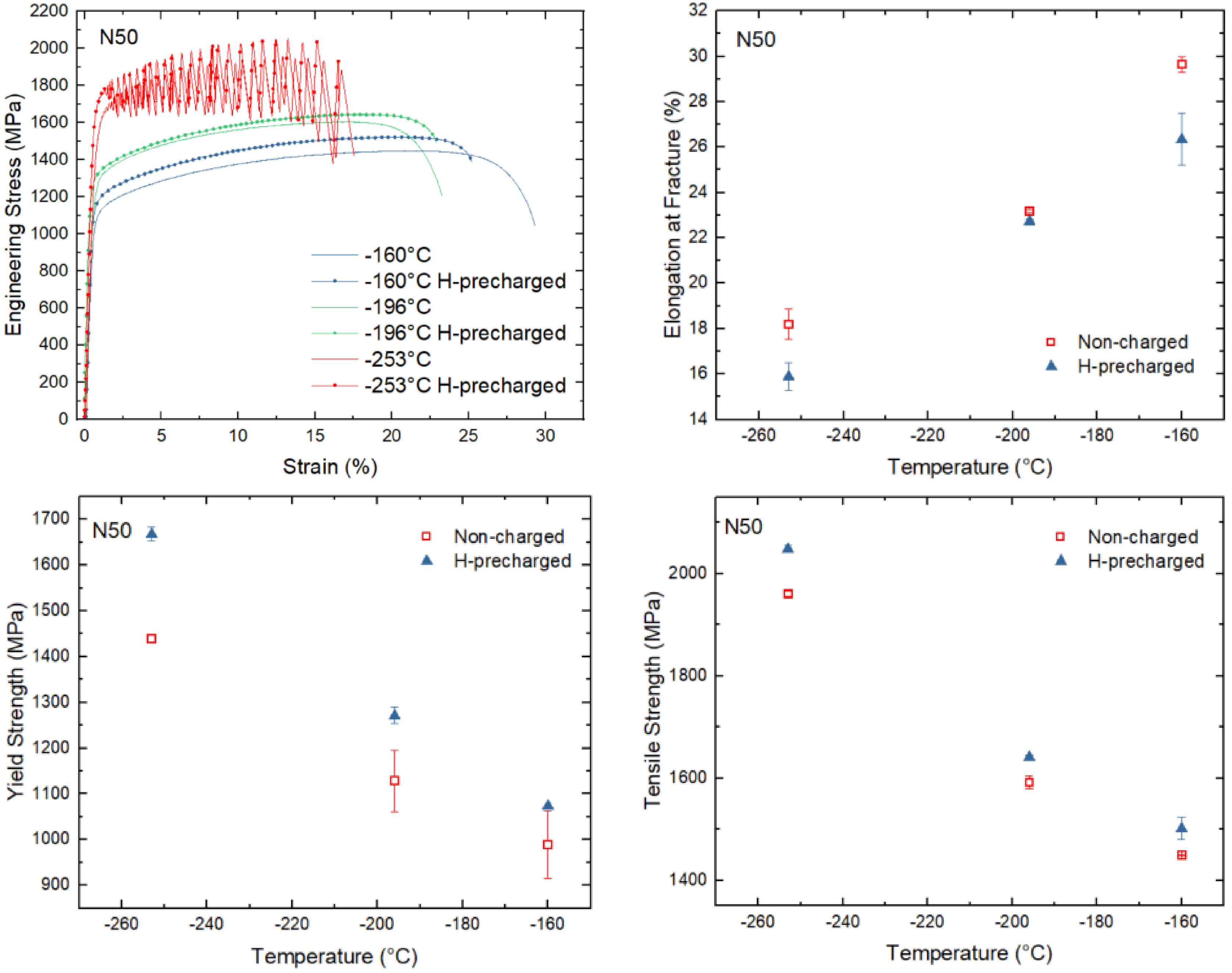
Nitronic 50 (XM-19) Baseline

- Annealed
  - 1065°C 30 min
  - Water quenched
- Increase in yield and ultimate stress with a decrease in temperature
- Reduced ductility below -80°C



Nitronic 50 (XM-19) Hydrogen Pre-charged

- Annealed
  - 1065°C 30 min
  - Water quenched



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Summary

- DOE – DOE goals are to increase on-board hydrogen storage capacity and to reduce the cost for storage. Cryogenic storage is one method to help meet those goals, but the cost in cryogenic systems, and materials of construction for storage systems to continue for reliability
- Resins – resins are a critical component for lightweight composite systems, but need to be carefully considered for outgassing, fracture toughness, and CTE
- Composites – composites provide reduced weight and high performance, but have a high cost, designs need to consider CTE liner limits, and composite microcracking from both thermal and stress cycling
- Modeling – high quality modeling can provide optimum design performance based on the filling profiles and construction design, but there is limited data below 77K for material performance for the models
- Metals – metal selection for liners should be considered carefully and tested. Assumptions of stainless steel are not affected by hydrogen are often incorrect. Materials should be carefully selected and tested with proper hydrogen exposure for fracture and fatigue to mitigate premature lifetime performance
- Welds – welds can be challenging for cryogenic service. The addition of hydrogen into the weld affected zone will impact the performance at cryogenic conditions and should be design appropriately for their limitations

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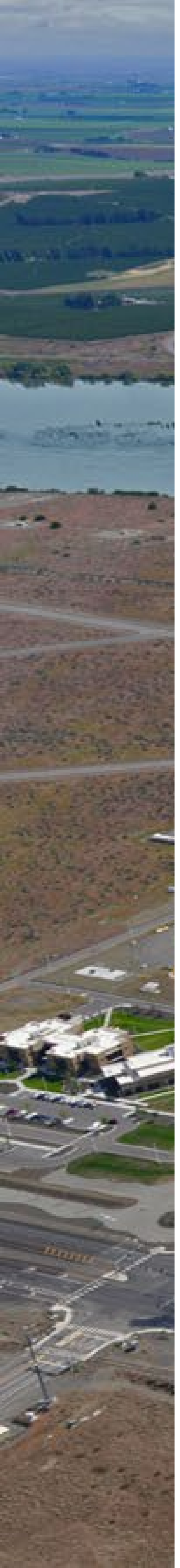

Thank you