Study Group on Materials Testing and Qualification for Hydrogen Service

Friday, July 19, 2019

Hyatt Regency San Antonio Riverwalk, ***Rio Grande E***
8:30am – 5pm

8:30	Opening Remarks and Introductions
Part I: Fracture mechanics-based design for hydrogen infrastructure	
	Bob Sims, *Open Discussion: Effect of hydrogen on the failure assessment diagram (FAD)*
	Chris San Marchi and Joe Ronevich, *Open Discussion: Prospects for life extension of high-pressure storage vessels*
	Joe Ronevich, *Materials performance in the presence of hydrogen-NG blends*
10:30	**Break**
Part II: Standardization	
	Hisao Matsunaga, *On the Plain- and Notched-fatigue in an Austenitic Stainless Steel — Similarity and Difference —*
	Jussi Solin, *Why smooth specimens of Austenite shall be tested under strain control*
	Chris San Marchi, *Methods of materials selection for hydrogen service*
12:00	**Lunch**
Part III: Materials and microstructure	
13:30	**Jinyang Zheng,** *Investigation on mechanical properties of S31603 austenitic stainless steel welded joint in 98 MPa gaseous hydrogen*
	Chris San Marchi, *Hydrogen effects on strain-induced phase transformation in austenitic stainless steels*
	Chris San Marchi, *DOE H-Mat consortium: Science-based advancement of materials for hydrogen technologies (time permitting)*
15:00	**Break**
Part IV: Test methods and testing capability	
	Paul Korinko, *Hydrogen studies at SRNL*
	Hyung-Seop Shin, *Characterization of hydrogen embrittlement sensitivity using in-situ SP test method*
	Toshio Ogata, *Influence of pressure on SSRT tests of solid and hollow specimens calculated by FEM analysis*
Free Discussion/Wrap-up	
17:00	Adjourn

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Life Extension of Tanks for High Pressure Storage Vessels

Chris San Marchi, Joe Ronevich

Sandia National Laboratories

Livermore, CA, USA

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July 19th, 2019

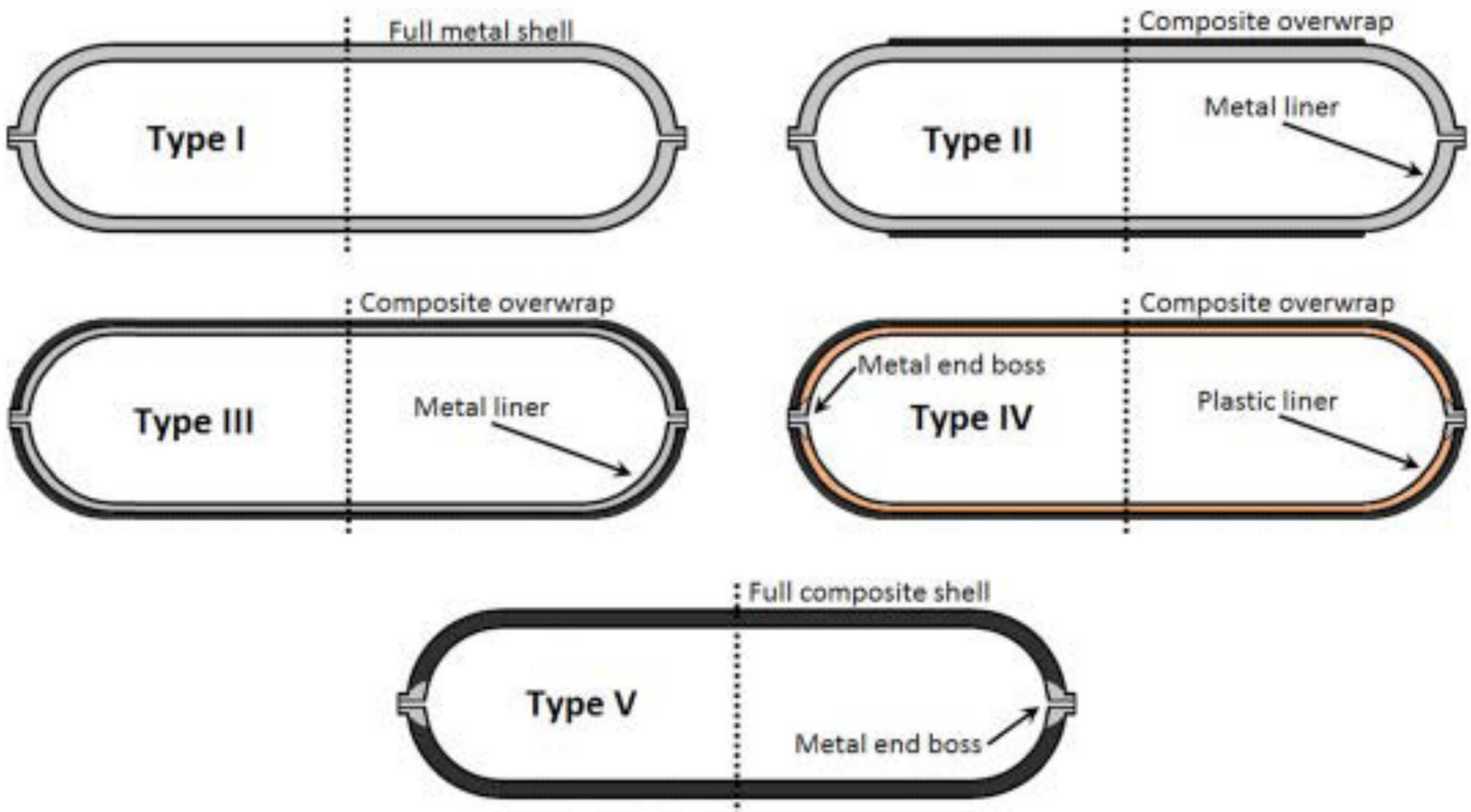
Numerous instances in reaching end of life criteria far sooner than anticipated

Design life: 37,500 cycles or 20 year (whichever comes first)

Pressure range: 13,500 psi (93 MPa) to 8,900 psi (61.3 MPa)

Reached cycle life in ~ 7 years!!!

Type II tanks - fiber-reinforced pressure vessels


Full metal shell
Type I
Composite overwrap
Metal liner
Type II
Composite overwrap
Type III
Metal liner
Composite overwrap
Metal end boss
Type IV
Plastic liner
Full composite shell
Type V
Metal end boss

Can life be extended of vessels?

What should count as a cycle?

- Should every pressure fluctuation count as a cycle?

- Define minimum ΔP (currently not well defined)

Identify and define inspection criteria

- Challenging as conventional NDE is not feasible on fiber reinforced tanks

How much life is left on these tanks?

- Presumably a lot, but how do we ensure this

What would inspection/recertification look like?

- Remove wrapping, inspect, re-wrap. → Not ideal or cost effective

- Need novel technique that is certifiable

Composite Overwrapped Pressure Vessels (COPV)

COPV Type II: composite-reinforced cylinder with load-sharing metal liner; normally termed hoop-wrapped. (Used in current work.)

Hydrogen Blending into Natural Gas

Joe Ronevich and Chris San Marchi

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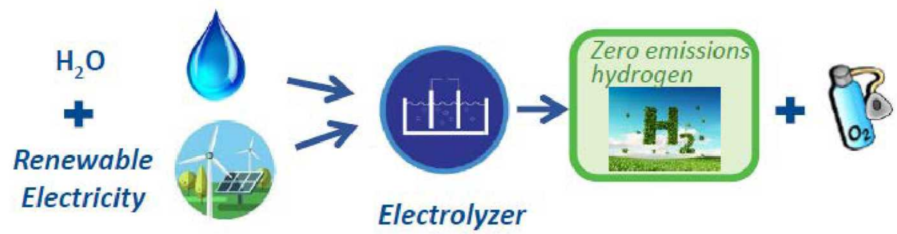
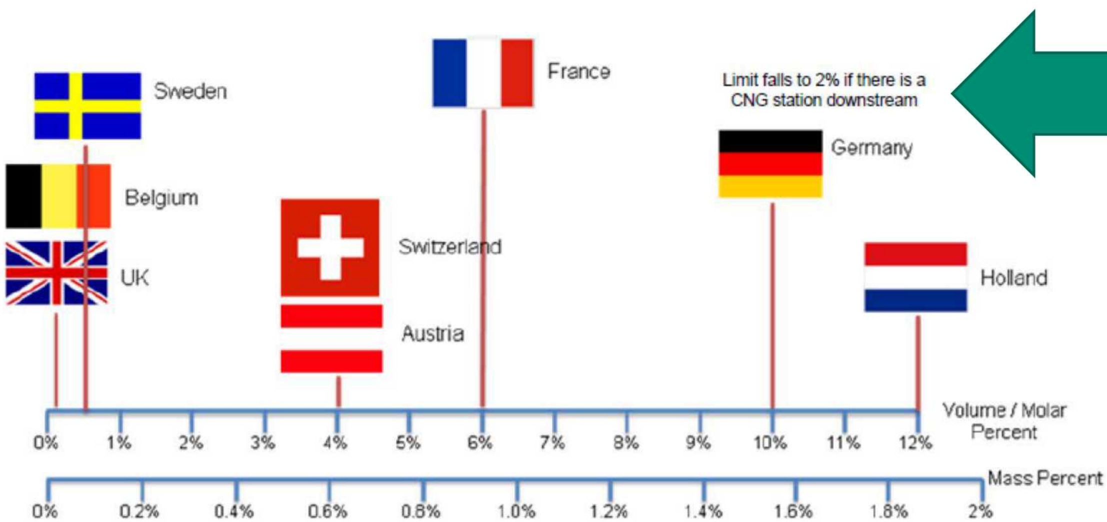
Growing interest in using hydrogen blends in natural gas to reduce carbon emissions

- Power-to-gas (P2G) using excess renewable electricity to produce hydrogen and inject into pipeline



EU Hydrogen Limits for Injection into the HP Gas Grid
Covered by a range of local laws and EU Directives



No harmonization of allowable hydrogen concentration in natural gas

Ref: George Minter, SoCal Gas "New Natural Gas Pathways for California: Decarbonizing the Pipeline" Presentation 2014.

Ref: SoCal Gas, "Hydrogen: Market Fundamentals, Trends and Opportunities", California Hydrogen Business Council, December 11, 2018.

Many demonstration projects are being performed around the world

France – Dunkirk **6% up to 20% H_2** into buses and 200 residential homes

Italy – Snam **5% H_2** into gas transmission network

UK – H21 Leeds CityGate Project – converting existing NG network to **100% H_2**

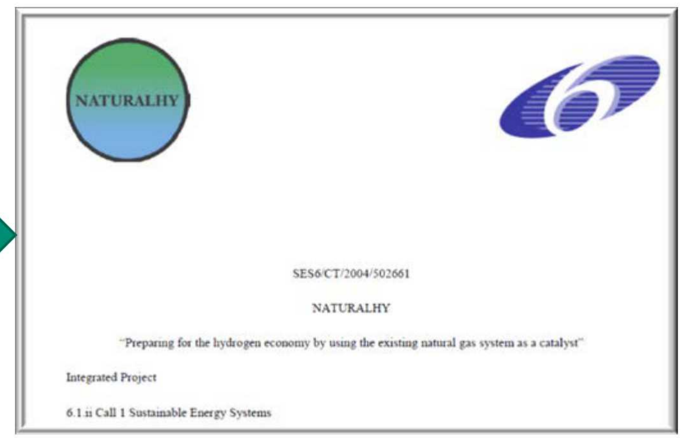
UK – HyDeploy at Keele University (up to **20% H_2** blend)

US – SoCalGas and UC Irvine – blending H_2 made from excess renewable electricity to campus pipeline

Germany – Trial of 170 customers supplied with up to **10% H_2** blend by E.ON Technologies

Netherlands – up to **20% H_2** blend injected in Amerland

Many references point to results from NaturalHy report, 2010


NATURALHY

SES6/CT/2004/502661

NATURALHY

"Preparing for the hydrogen economy by using the existing natural gas system as a catalyst"

Integrated Project

6.1.ii Call 1 Sustainable Energy Systems

https://www.engie.com/en/businesses/gas/hydrogen/power-to-gas/the-grhyd-demonstration-project/
https://www.azernews.az/region/148145.html
https://www.northerngasnetworks.co.uk/wp-content/uploads/2017/04/H21-Report-Interactive-PDF-July-2016.compressed.pdf
https://www.elp.com/articles/2016/12/socalgas-uc-irvine-test-hydrogen-energy-technology-to-store-renewable-energy.html

So how much hydrogen is allowed in natural gas?

A) 2%?

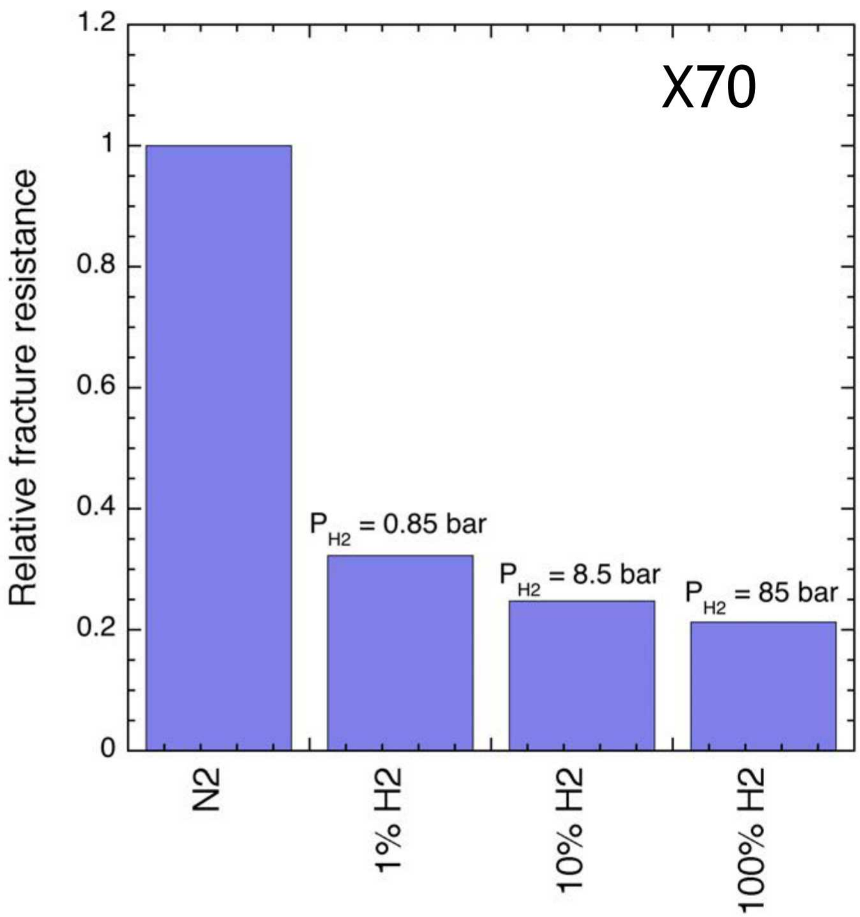
B) 5%?

C) 10%?

D) It depends on your operating conditions and your definition of the word "allowed".

Often times these values (2,5,10% H_2) are based on performance of burners, not measurements of material compatibility with hydrogen

Low pressure H_2 has substantial effect on fracture resistance of pipeline steels

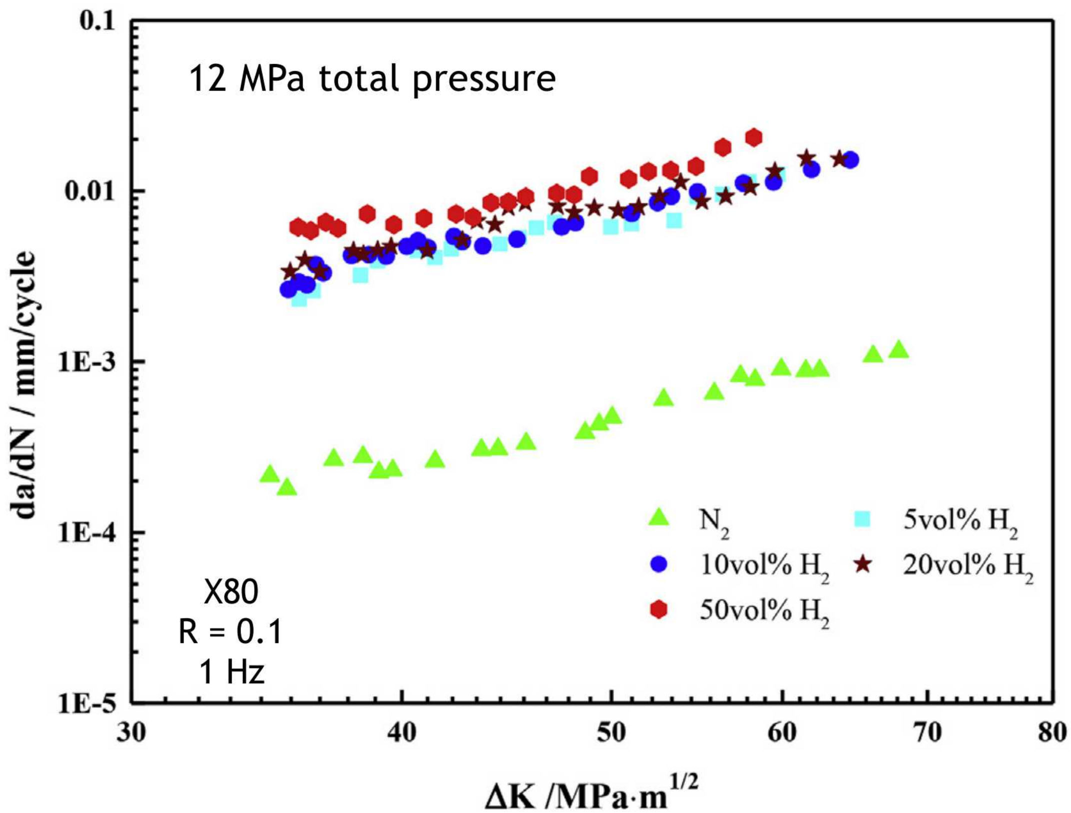


From: Briottet et al, ASME PVP-2018 conf.

- **Measurements of fracture resistance in gaseous mixtures of H2 and N2 show substantial effects of H2**
- **1% H2 is only modestly different than 100% H2**
- **Total pressure = 85 bar**

<1 bar of H2 reduces fracture resistance

Low pressure H_2 has substantial effect on fatigue crack growth of pipeline steels

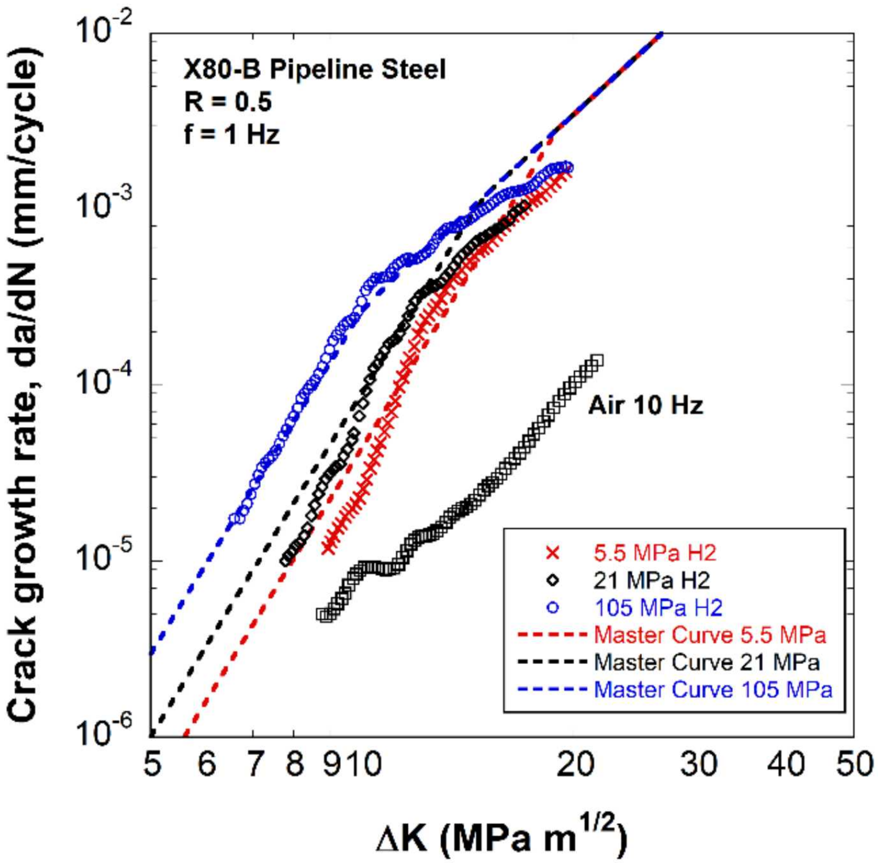


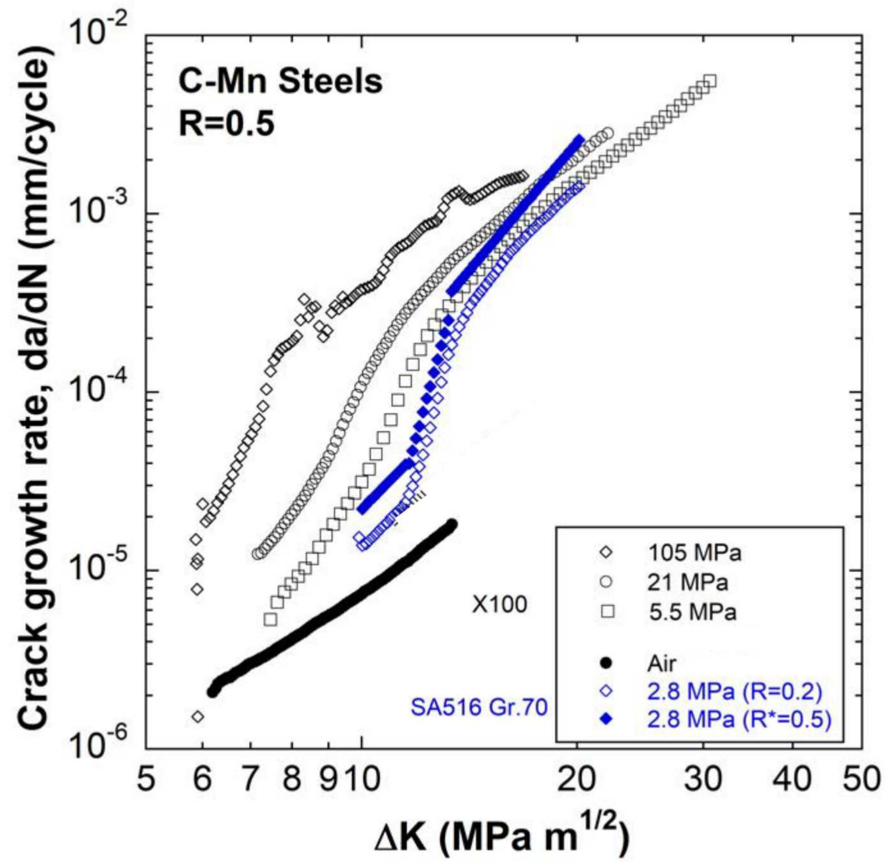
From: Meng et al, *IJ Hydrogen Energy* **42** (2017) 7404.

- **Measurements in gaseous mixtures of H2 and N2 show acceleration of fatigue crack growth rate with 5% H2**
  - **But little additional acceleration with higher H2 content**

Small amounts of hydrogen can have substantial effect on fatigue and fracture

In lower ΔK range, lower pressures still exhibit sizeable increases in FCGR

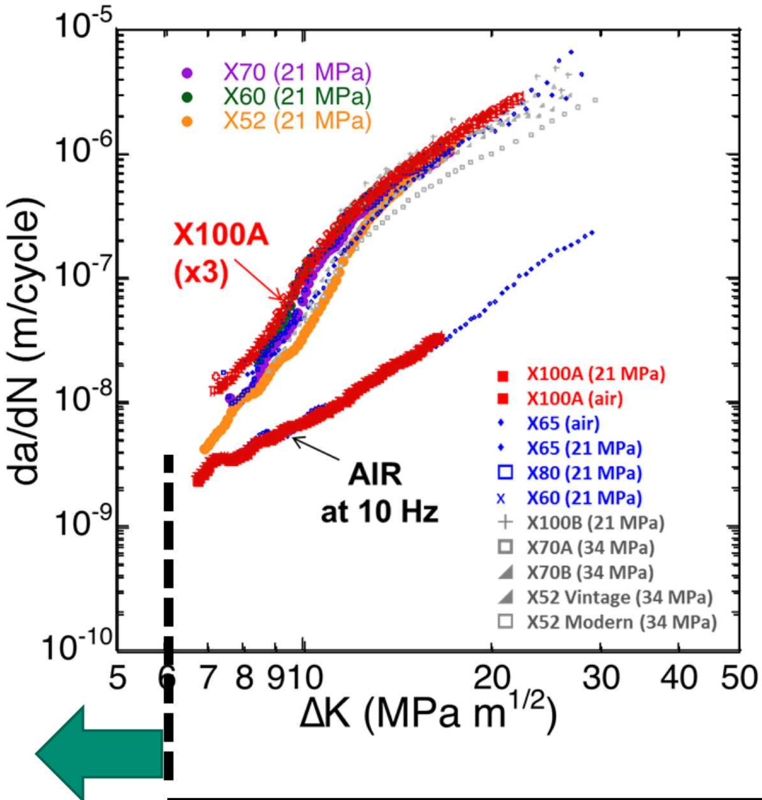




SNL data (taken from various published and unpublished)

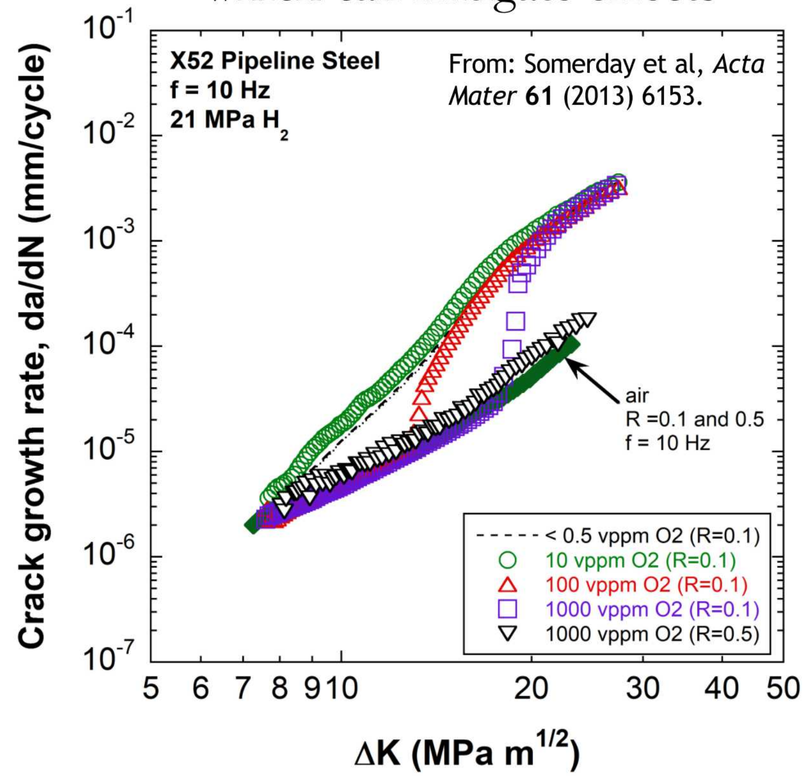
How to reduce effects of hydrogen degradation in blended pipelines from HA-FCG?

1) Design / operate conservatively



Ensure that operating envelope is at low ΔK where curves converge

2) Make use of impurities which can mitigate effects



Impurities in H_2 can have substantial effects on in-service performance

Natural Gas streams contain impurities such as Oxygen

- Maximum allowable levels of oxygen range from 0.1 to 0.2% (1000 – 2000 vppm)

→ Well above what is needed to mitigate HA-FCG (in specific operating conditions)

Typical Composition of Natural Gas

Methane	CH_4	70-90%
Ethane	C_2H_6	
Propane	C_3H_8	0-20%
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne, Xe	trace

However, these are maximums NOT minimums so can they guarantee a minimum level of oxygen?

http://naturalgas.org/overview/background/

Summary: The role of mixed hydrogen gas environments and impurities should be considered carefully

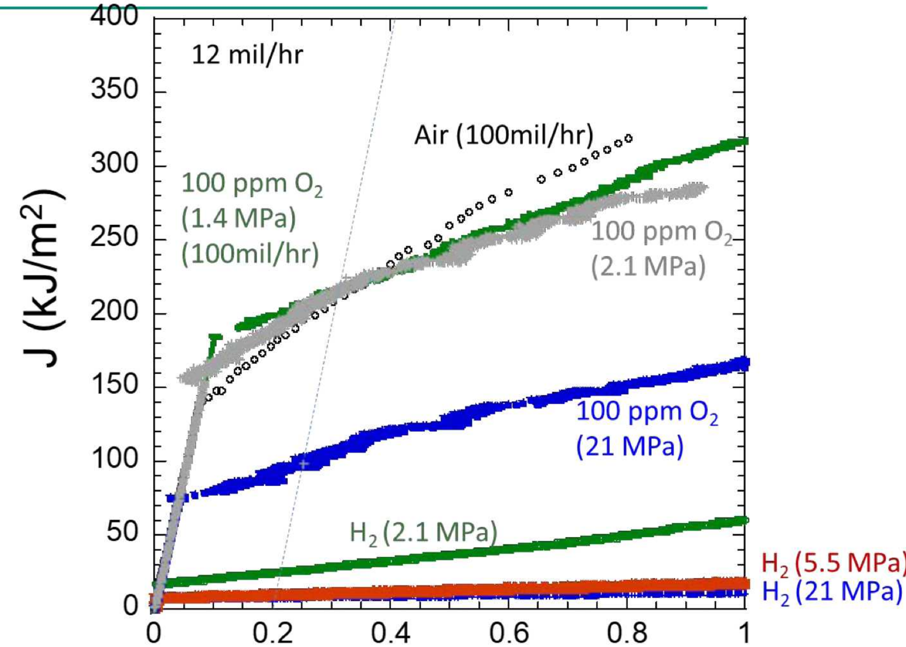
- Small partial pressure of gaseous H2 can have substantial effects on fracture and fatigue of steels
- Oxygen can mitigate effects of H2 in ferritic steels
  - Sensitive to mechanical and environmental variables
  - Other passivating species can have similar effects
- Structural integrity of pipelines carrying mixed gases will depend sensitively on the details
  - NG has many impurities, which can mitigate H2 effects
  - Pure methane is inert and even small additions of H2 can be significant

Materials compatibility for hydrogen containment structures depends on the application and the design

Back up slides

Oxygen moderated hydrogen-assisted fracture

- In 21 MPa pure H_2, fracture toughness K_{JIH} values decreased by 80%.
- In 21 MPa mixed gas, fracture toughness decreased by only 30%.
- At lower pressures (1.4-2.1 MPa) in mixed gas, no effect of hydrogen was measured (e.g. K_{JIH} in air ~ K_{JIH} in mixed gas
- At lower pressure, test rates of 0.3 and 2.5 mm/hr resulted in similar K_{JIH} ~ air



Sample ID	Environment	Test Pressure (MPa)	Actuator rate (mm/hr)	da/dt (mm/s)	K_{JIH} (MPa $m^{1/2}$)
X100-5	H2	21	0.3	8.5E-4	43
X100-6	H2	5.5	0.3	3.6E-4	47
X100-7	H2	2.1	0.3	1.7E-4	75
X100-51	Air	-	2.5	5.0E-4	217
X100-52	Air	-	2.5	1.4E-4	202
X100-53	H2 + 100 ppm O2	21	0.3	1.1E-4	151
X100-55	H2 + 100 ppm O2	2.1	0.3	7.4E-5	222
X100-56	H2 + 100 ppm O2	1.4	2.5	1.0E-4	222

Lower pressure fracture toughness similar to tests in air

Ronevich, PVP2019

NaturalHy report states…

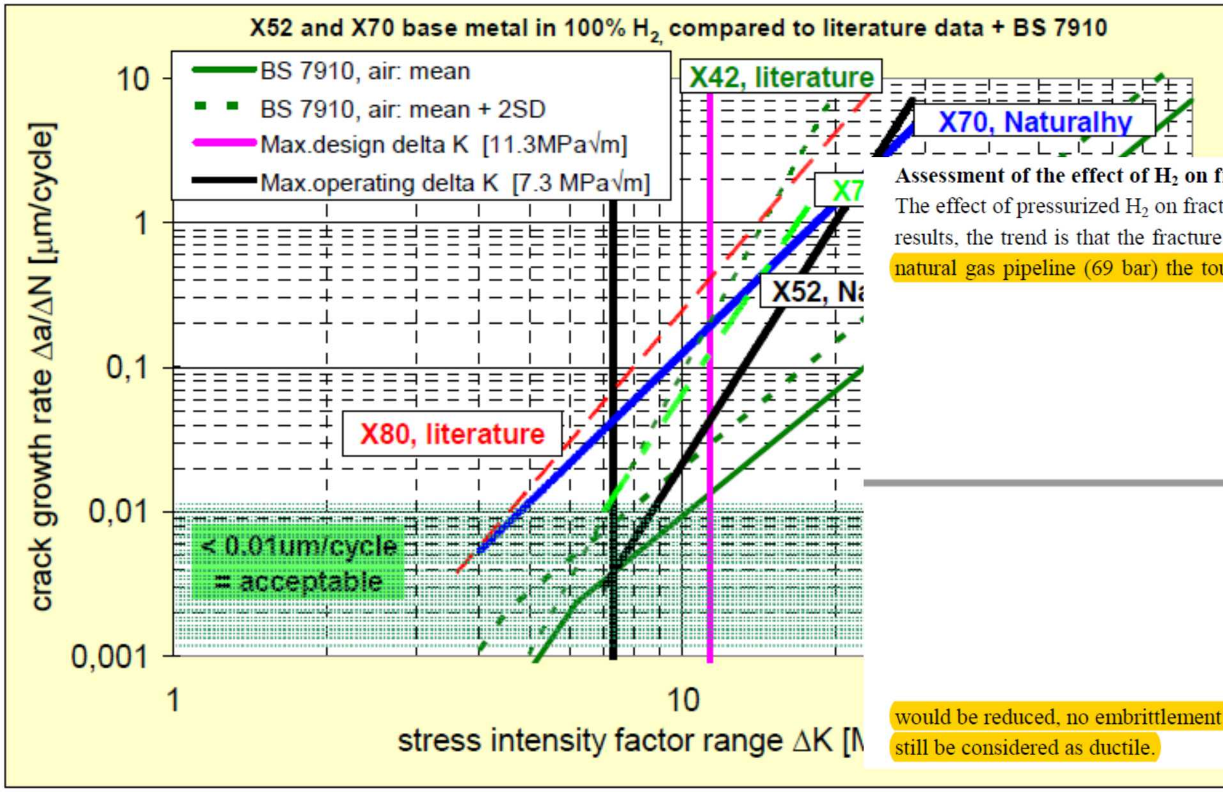


Figure 5.1 Fatigue crack growth of X52 and X70 base materials in 100% H_2.

Assessment of the effect of H_2 on fracture toughness of steels

The effect of pressurized H_2 on fracture toughness performance is not fully clarified yet. Although wide variation results, the trend is that the fracture toughness decreases with increasing H_2 pressure. At a typical pressure of a natural gas pipeline (69 bar) the toughness can decrease by 30 -50%. However, even if the fracture resistance

28

would be reduced, no embrittlement was noticed, and the mechanical behaviour of the X52 and X70 steels can still be considered as ductile.

Reports often focus on performance of burners rather than Material Compatibility

Hydrogen effects on strain-induced phase transformation in austenitic stainless steels

Chris San Marchi,
Sandia National Laboratories

Study Group meeting
July 19, 2019

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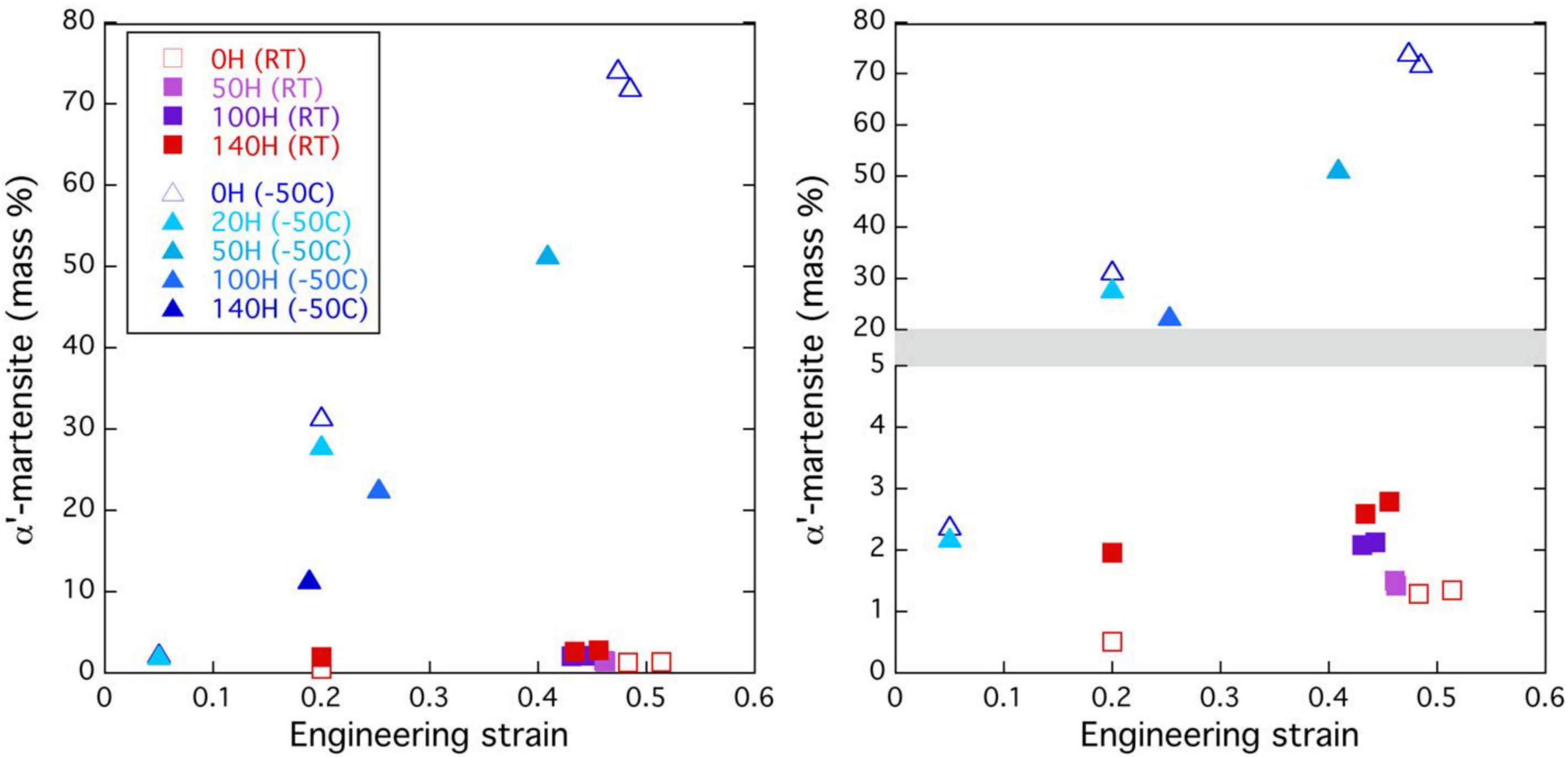
Austenitic stainless steels

Designation	Fe	Cr	Ni	Mn	Mo	Si	C	N	S	P
304L	Bal	19.64	10.6	1.62	–	0.65	0.028	0.04	0.0042	0.02
316L	Bal	16.75	12.68	0.64	2.8	0.62	0.020	0.04	0.0023	0.008
XM-11 - F	Bal	21.06	7.16	9.11	–	0.53	0.031	0.28	0.001	0.015
XM-11 - A	Bal	19.27	6.82	9.03	–	0.39	0.022	0.25	<0.001	0.017

F= forged; A = annealed

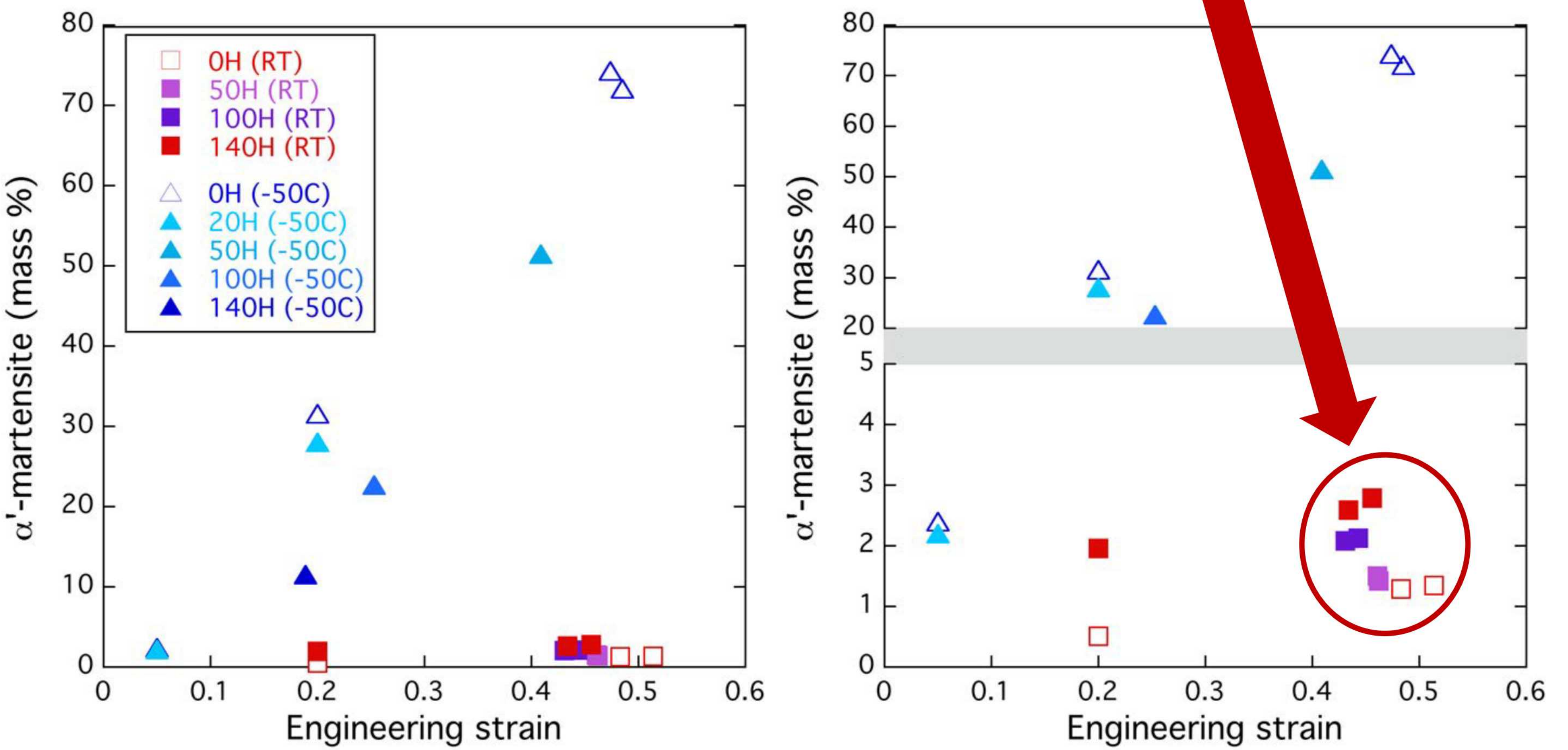
Designation		YS (MPA)	TS (MPa)	EL (%)	RA (%)
304L	Metastable	436	611	69	85
316L	Metastable	422	571	70	84
XM-11 - F	stable	674	830	48	76
XM-11 - A	stable	457	755	65	83

Strain-induced α'-martensite transformation in 304L



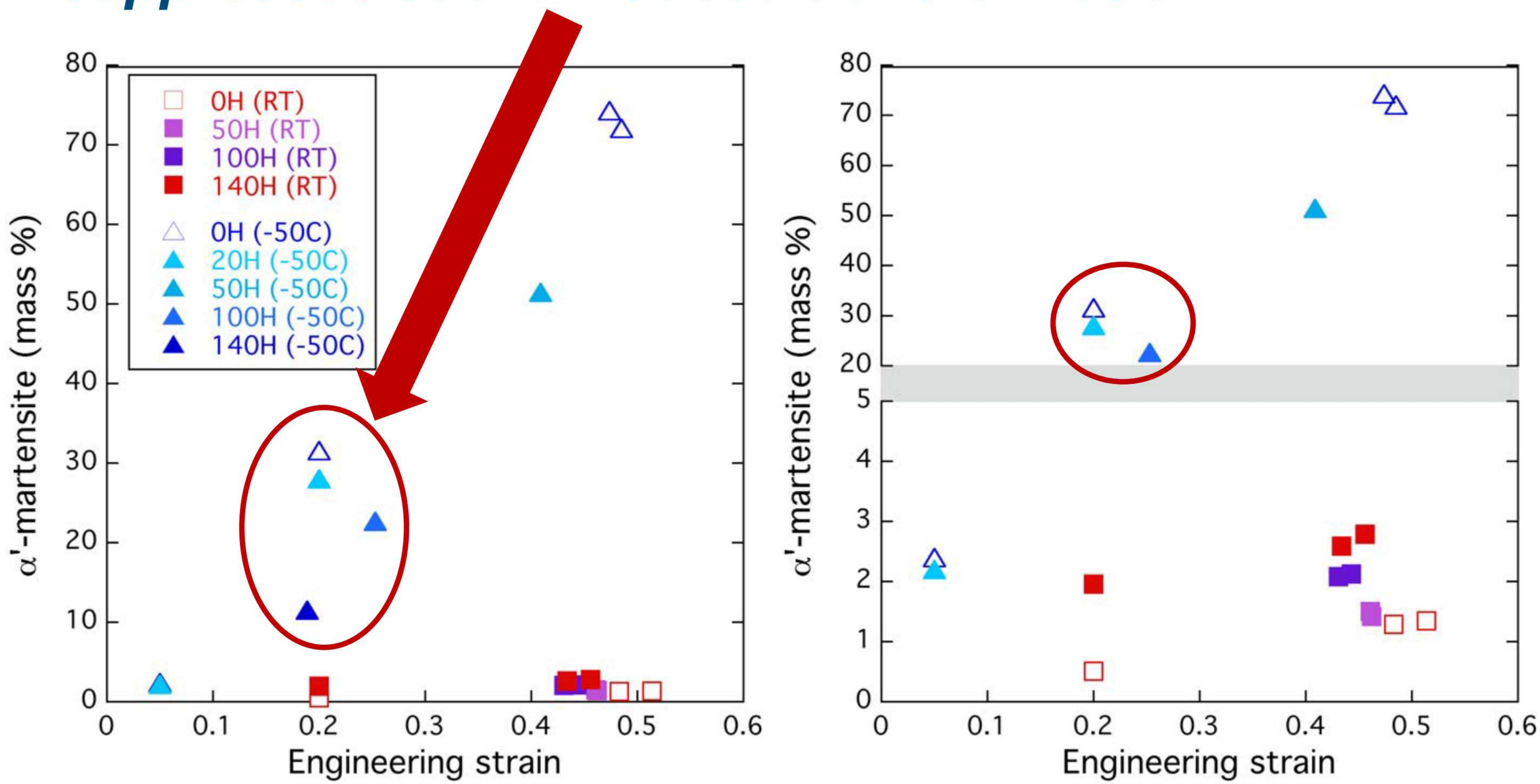
Strain-induced α'-martensite transformation in 304L

At *low* volume of transformation, hydrogen *promotes* strain-induced transformation

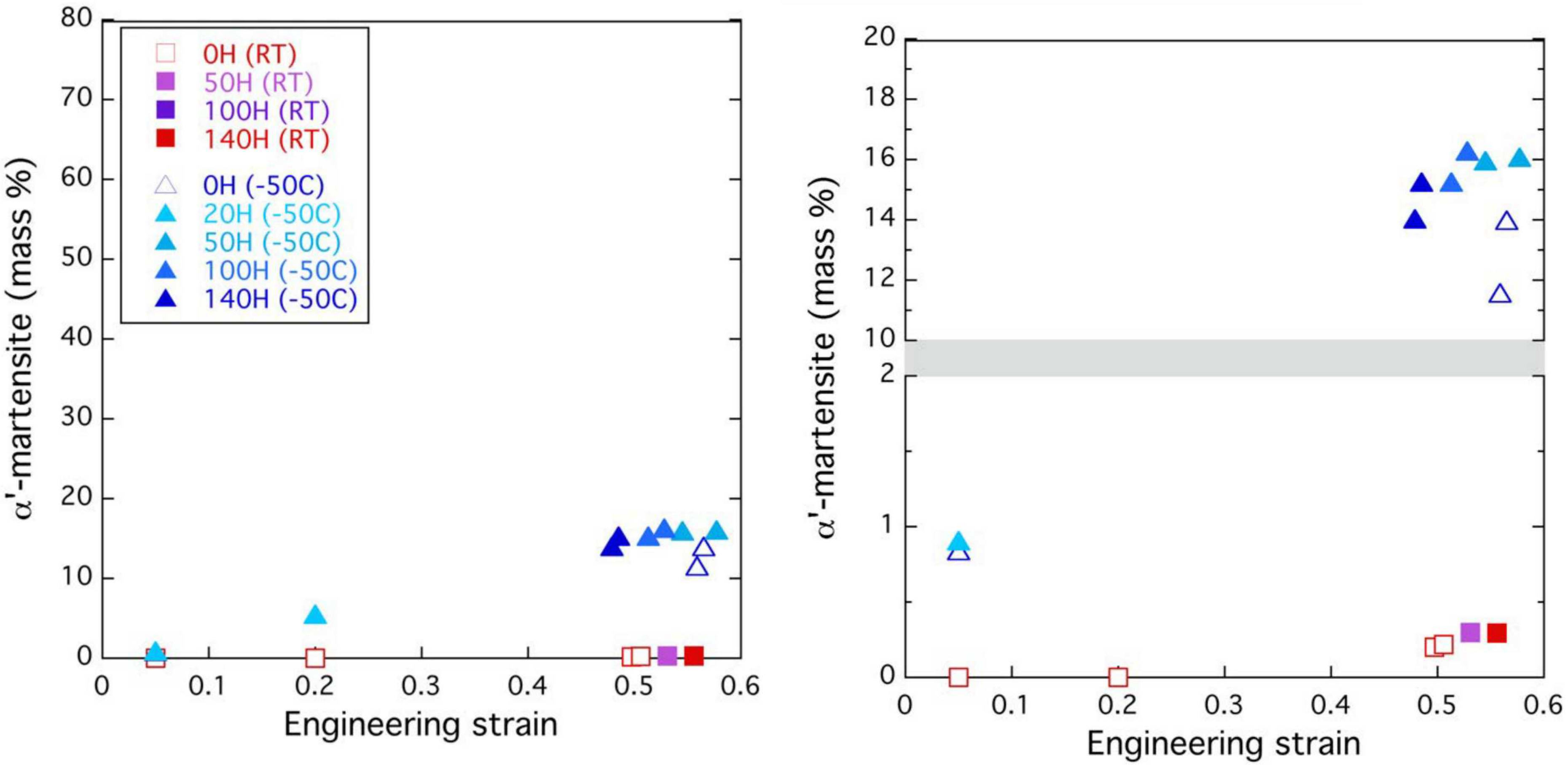


Strain-induced α'-martensite transformation in 304L

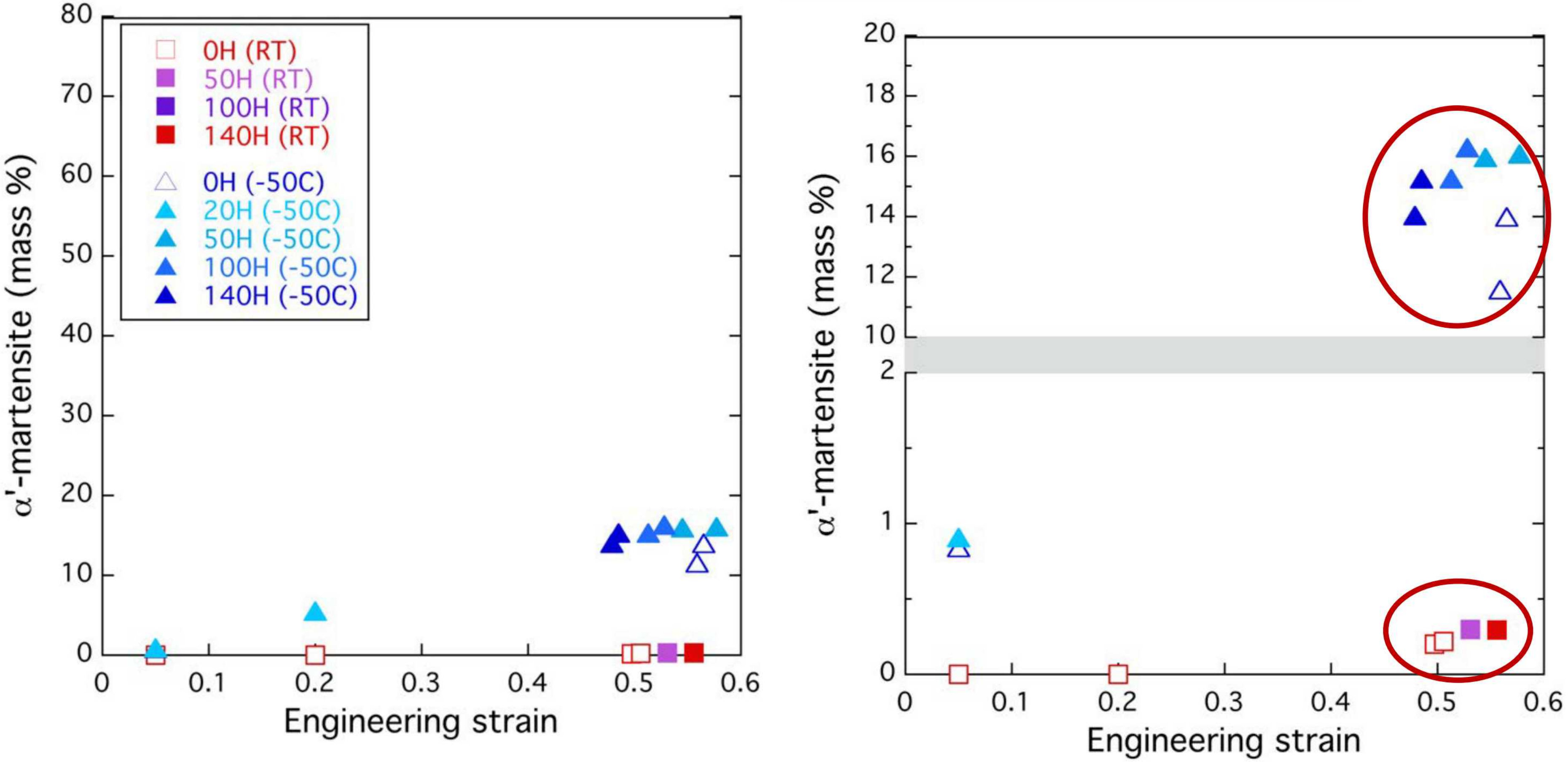
At *high* volume of transformation, hydrogen *suppresses* strain-induced transformation



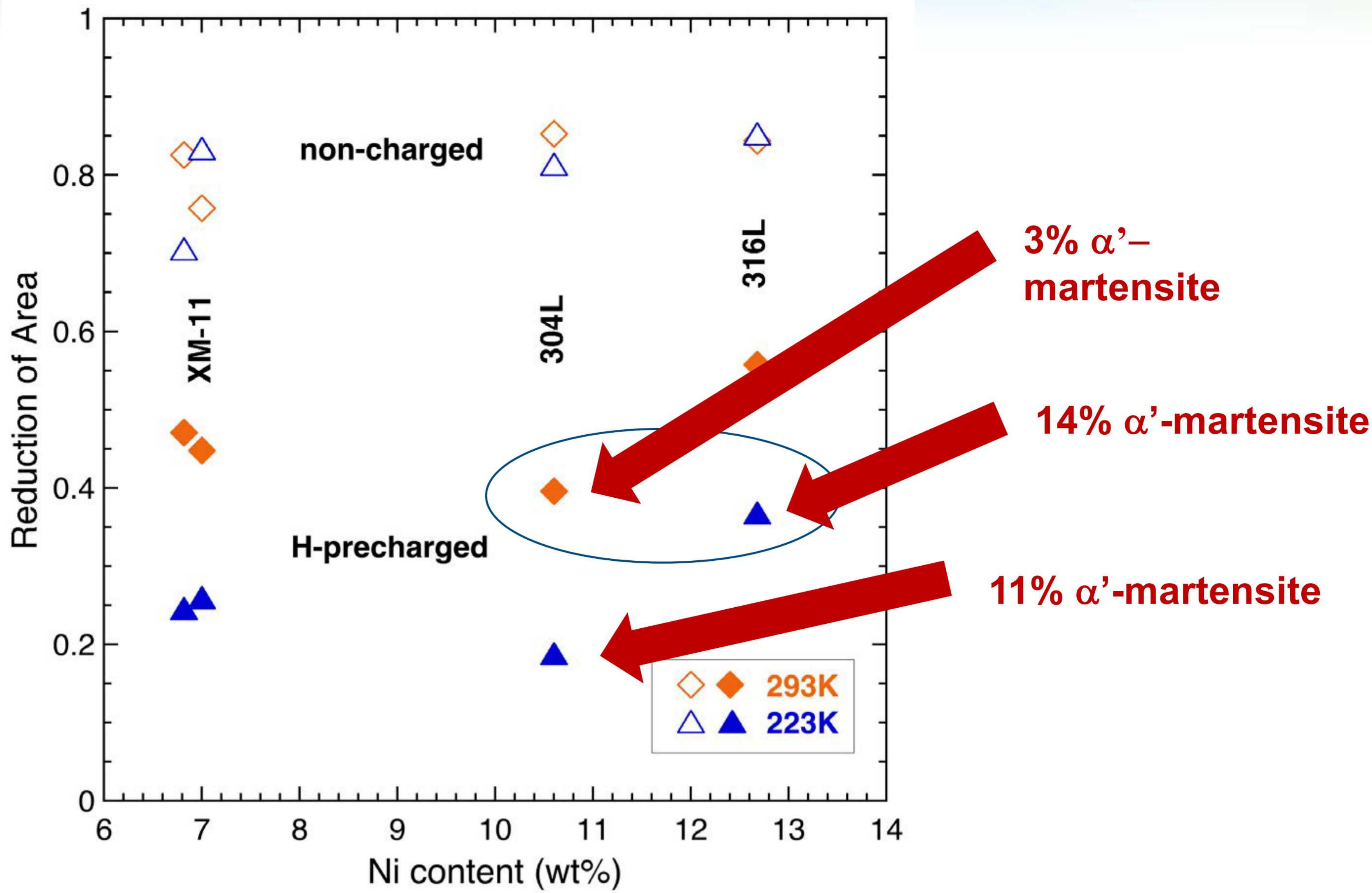
Strain-induced α'-martensite transformation in 316L



Strain-induced α’-martensite transformation in 316L



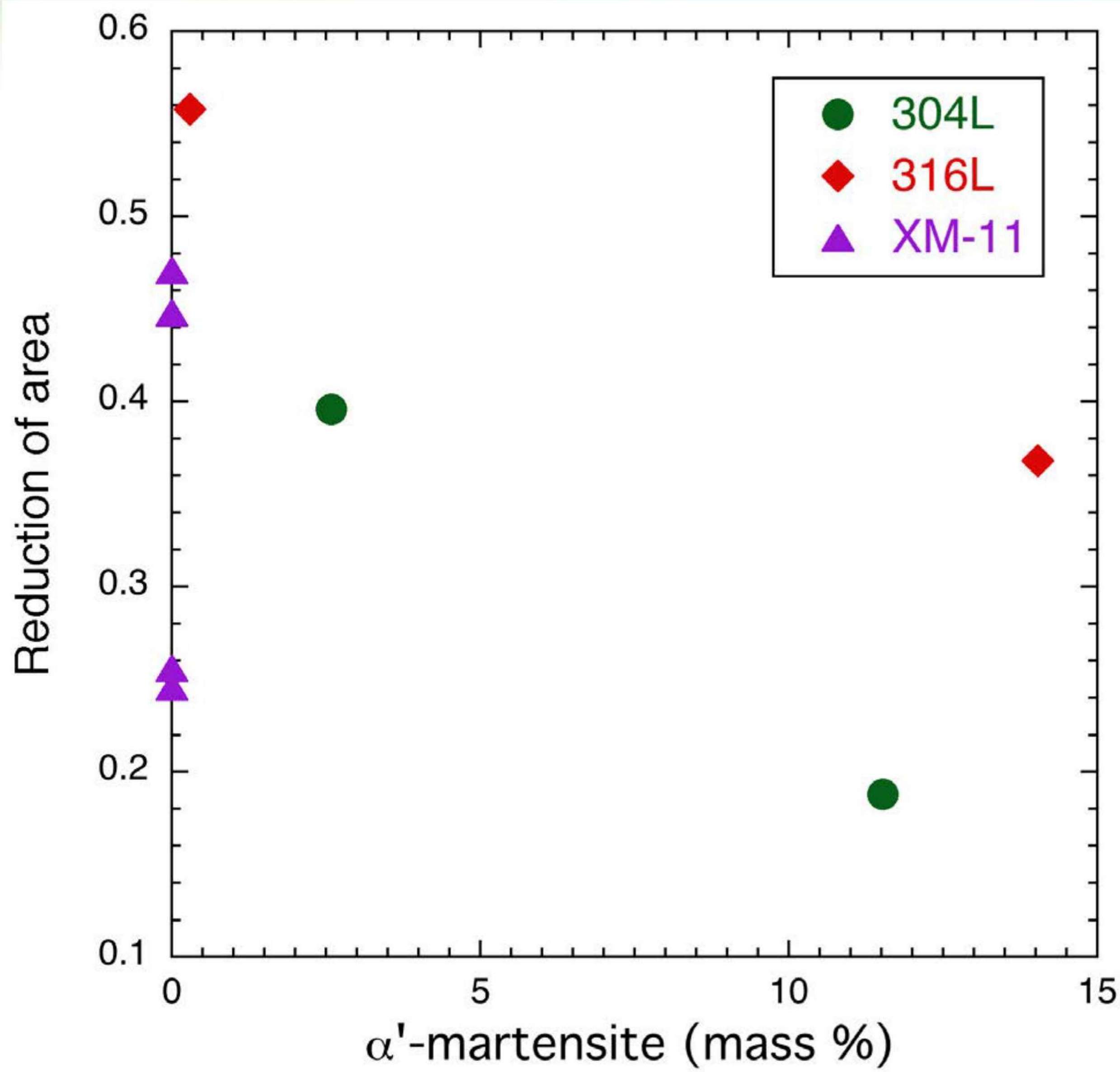
Ductility of austenitic stainless steels with internal hydrogen



Summary of observations

- Hydrogen promotes strain-induced α'-martensite when volume of martensite is small (<20%)
- Hydrogen suppresses strain-induced α'-martensite when volume of martensite is large (>20%)
- No apparent correlation between α'-martensite and ductility with internal H

Ductility of austenitic stainless steels with internal hydrogen



Strength and ductility as a function of hydrogen content