ASME

SETTING THE STANDARD

Material Testing Priorities for H2 Infrastructure

ASME/SRNL Materials and Components for Hydrogen Infrastructure Codes and Standards Workshop

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Topics

- ASME Pressure Boundary Needs
- Tests and Data Requirements
- Research Needs
- Recent Testing By SECAT, Inc. and Sandia Lab

What We Need to Know About Materials Used for Pressure Boundary Construction

- The context of the pressure boundary construction is for hydrogen delivery systems after production, which is expected to include hydrogen pressures from full vacuum to 1000 bar (15,000 psi) and temperatures from liquid to 150ºC (300ºF).
- The most common materials being used for current and planned construction are carbon steel (for pipelines) and Type 316 stainless steel (for piping). Hence, the high priority testing should be done on carbon steel and Type 316 stainless steel. Testing of other metals such as aluminum alloy 6061-T6 and Type 304 stainless steel should be done as a second priority.

Carbon Steels with Yield Strengths up to 360 MPa (52,000) psi

- **Baseline Testing** of C-Mn, C-Mn-Microalloy (HSLA), and C-Mn-Alloy steels used in pipeline and piping systems for the transportation of high purity hydrogen gas needs to proceed.
- Samples representing various levels of chemistry (C, Mn, microalloy, solute alloy, etc.) typical of what is used in the current pipeline and piping systems needs to be evaluated. More importantly these samples should have a range of microstructural differences in ferrite, pearlite, acicular ferrite, bainite, martensite, etc. By choosing various C-Mn and microalloy/solute alloy samples the testing should yield a variety of microstructures with various volume fractions of any one microstructural constituent. Grades that can be considered are:
- A53, A106, A134 and API grades X42-52 from current production as well as pipe material that has been in hydrogen or natural gas service for over 20 years (metallurgy has been evolving over the years and therefore not all API grades are created equal in regard to their ability to perform in hydrogen service).

Tests and Data Requirements C-Mn and Microalloy Steels

	Need to Know*	Current Knowledge?
Base Metal	Reduction in ultimate strength	Reductions are reported
	Reduction in yield strength	Reductions are reported
	Reduction in ductility	Significant reductions have been measured
	Fracture resistance (K_{IH} values)	Mostly unknown
	Fatigue resistance (da/dn values)	Mostly unknown
	What changes when the material is cold formed	Unknown
	How does a corroded surface affect the performance?	Unknown
	Diffusion coefficients for various microstructures and the amount of hydrogen that gets trapped in the matrix	Unknown?
Weld Metal	Reduction in ultimate strength	Unknown
	Reduction in yield strength	Unknown
	Reduction in ductility	Unknown
	Fracture resistance (K_{IH} values)	Unknown
	Fatigue resistance (da/dn values)	Unknown
	Effect of post weld heat treatment	Unknown
Heat Affected Zone	Reduction in ultimate strength	Unknown
	Reduction in yield strength	Unknown
	Reduction in ductility	Unknown
	Fracture resistance (K_{IH} values)	Unknown
	Fatigue resistance (da/dn values)	Unknown
	Effect of post weld heat treatment	Unknown

Tests and Data Requirements

Testing Environment

- The immediate information need is over the range of pressures up to 200 bar (3,000 psi) and temperatures from ambient to 150ºC (300ºF). As a second priority, information about increasing pressures up to 1000 bar (15,000 psi) is needed to determine the practical upper limit for use of carbon steel. The samples should be tested under different environmental conditions. This includes various pressures, temperatures and exposure times, unless these can be shown to be unimportant variables.

Information to be Captured Includes

- Complete chemistry characterization.
- Complete microstructural characterization including volume fractions of each microstructural constituent, degrees of banding, cleanliness (inclusion size, frequency and shape), voids, cracks, grain size, dislocation/residual stress analysis, etc.
- The product form from which the specimens were taken.
- The product form production process, including either hot or cold forming.
- Any thermal treatments of the product or Mechanical forming (bending).
- The preparation of the test specimens, including operations such as cutting, grinding, machining, flattening, bending, weld procedure used for sample fabrication, thermal treating, hydrogen charging and the lab environment.

Tests and Data Requirements Stainless Steels

- Testing of stainless steels in high purity hydrogen needs to proceed to support the current assumption that stable grades of austenitic stainless steels behave well in hydrogen environments. The assumption is based on a long history of using stainless steel for hydrogen service, but almost all of the experience is for piping and equipment operating a pressures much lower than 1000 bar (15,000 psi).

<u>Samples to be tested</u>

- Most Type 316 stainless steels are dual certified; i.e. they meet the specification requirements for both the traditional and low carbon grades. Samples to be tested should be dual certified or a combination of traditional and dual certified grades.

Tests and Data Requirements Stainless Steels

	Need to Know*	Current Knowledge?
Base Metal	Reduction in ultimate strength	Modest reductions are reported
	Reduction in yield strength	Modest reductions are reported
	Reduction in ductility	Modest reductions are reported
	Fracture resistance (K_{IH} values)	Unknown
	Fatigue resistance (da/dn values)	Unknown
	What changes when the material is cold formed	Unknown
	Diffusion coefficients for various microstructures and the amount of hydrogen that gets trapped in the matrix	Unknown?
	Effect of alloy shaving	Unknown?
Weld Metal	Reduction in ultimate strength	Unknown
	Reduction in yield strength	Unknown
	Reduction in ductility	Unknown
	Fracture resistance (K_{IH} values)	Unknown
	Fatigue resistance (da/dn values)	Unknown
Heat Affected Zone	Reduction in ultimate strength	Unknown
	Reduction in yield strength	Unknown
	Reduction in ductility	Unknown
	Fracture resistance (K_{IH} values)	Unknown
	Fatigue resistance (da/dn values)	Unknown

Tests and Data Requirements Stainless Steels

- The practice of "alloy shaving" we needs to be investigated. The affect of alloy content (austenite formers) must be determined to verify that current chemistry ranges are adequate for hydrogen service at high hydrogen pressures.
- Additionally we need to verify the affects of strain (cold work) on the same alloys. The martensite transformation needs to be evaluated to determine if large strains, over 10%, have a detrimental effect on austenitic stainless steel resistance to hydrogen embrittlement at high hydrogen pressures.
- Welding of stainless must also be investigated and delta ferrite content correlated against weld performance at high hydrogen pressures.

Tests and Data Requirements

<u>Testing Environment</u>

- The information is needed over the range of pressures up to 1000 bar (15,000 psi) and temperatures from liquid to 150ºC (300ºF). The samples should be tested under different environmental conditions. This includes various pressures, temperatures and exposure times, unless these can be shown to be unimportant variables.

<u>Information to be Captured Includes</u>

- Complete chemistry characterization.
- Complete microstructural characterization including volume fractions of each microstructural constituent, degrees of banding, cleanliness (inclusion size, frequency and shape), voids, cracks, grain size, dislocation/residual stress analysis, and percent ferrite.
- The product form from which the specimens were taken.
- The product form production process, including either hot or cold forming.
- Any thermal treatments of the product. Mechanic
- The preparation of the test specimens, including operations such as cutting, grinding, machining, flattening, bending, weld procedure used for sample fabrication, thermal treating, hydrogen charging and the lab environment.

Fatigue in A Hydrogen Environment

- Hydrogen gas enhances the fatigue crack growth rate of carbon steels. The fatigue crack growth rates in hydrogen become increasingly greater relative to crack growth rates in air or inert gas as ΔK increases. In the higher range ofΔK, fatigue crack growth rates are at least ten-fold greater than crack growth rates in air or inert gas. While the da/dN vs ΔK relationships in air and inert gas are remarkably similar, the da/dN vs ΔK relationships in hydrogen are noticeably more varied.

In the higher range of ΔK, crack growth rates in hydrogen can vary by more than a factor of 10.

The da/dN vs ΔK relationships in hydrogen gas can be affected by numerous variables, including gas pressure, load ratio, load cycle frequency, and gas composition.

Ref. Sandia Report:

Technical Reference on Hydrogen Compatibility of Materials

Carbon Steels: C-Mn Alloys (code 1100)

Prepared by: B.P. Somerday, Sandia National Laboratories

Editors:C. San Marchi, B.P. Somerday; Sandia National Laboratories

More test data needed

Effect of gas pressure

- Fatigue crack growth rates generally increase as hydrogen gas pressure increases

Effect of load cycle frequency

- Fatigue crack growth rates in hydrogen gas generally increase as the load cycle frequency decreases.

Effect of gas composition

- Additives to hydrogen gas can reduce fatigue crack growth rates, however this phenomenon has not been explored at low load cycle frequencies.

Testing

- The preceding has shown what is being done, what information is lacking and what results we need to support our code writing activities.
- What testing activities and how the tests are run and documented needs to be a joint agreement with engineers involved in the codes and testing labs.
- Standardization of testing and documentation must be accomplished. Data from all test labs must be able to be correlated with one-another.
- Test results must be archived in a central location with access for all SOD’s.

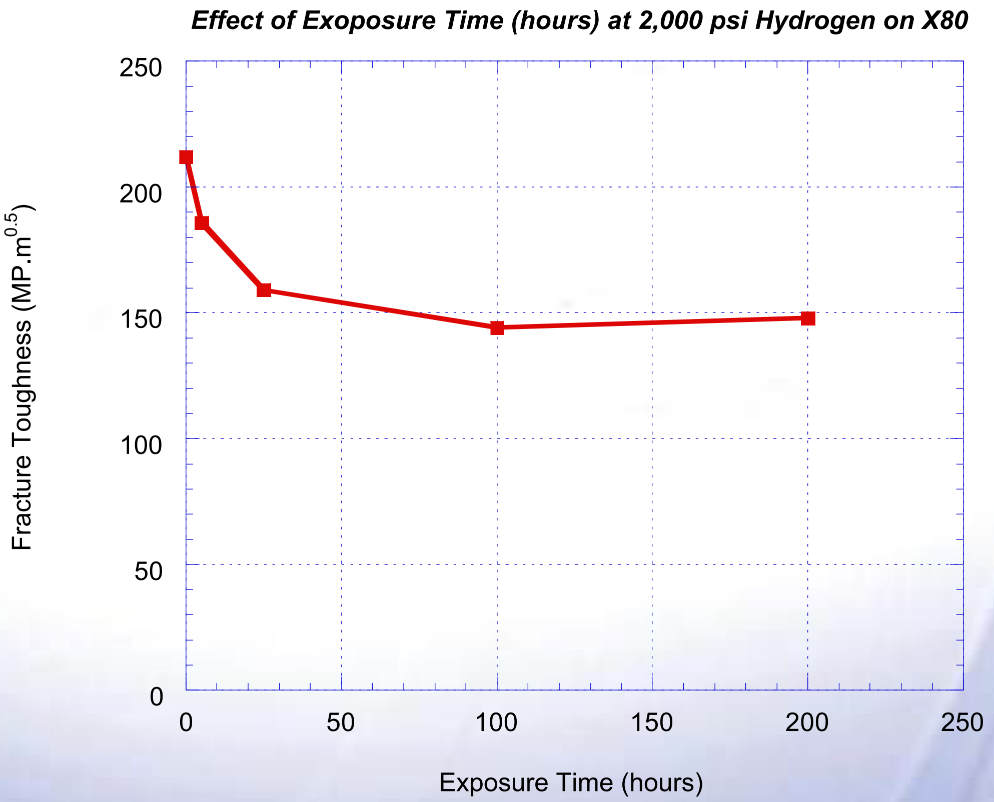
Summary of ABI Measured Mechanical Properties of Selected Steels

Sample ID	YS	Calc. Eng.	Calc. Unif.	YS/UTS
All API Plate Samples	(ksi)	UTS	Ductility	Ratio
		(ksi)	(%)	
API X70, A-1	82.8	102.3	7.9	0.81
API X70, A-2	82.3	101.3	7.8	0.81
API X70, A-3	81.4	100.9	8.0	0.81
API X80, B-1	74.9	93.4	8.1	0.80
API X80, B-2	75.0	94.7	8.3	0.79
API X80, B-3	77.4	94.3	7.6	0.82
API X80, C-1	86.4	104.8	7.5	0.82
API X80, C-2	84.8	104.5	7.9	0.81
API X80, C-3	86.2	105.9	7.6	0.81

In-Situ SSM Testing System - Effects of 2,000 psi Hydrogen on the ABI-Measured Mechanical Properties as a Function of Exposure Time

X80 Cond.	YS (MPa)	UTS (MPa)	ABI-Hardness (030G)	Stren. Coeff., K (MPa)	Strain-Hard. Exp., n	Critical Stress (MPa)	Crit. Depth, ht (mic)	KJc ($MPa.m^{0.5}$)	Red. in KJc
AR	651	810	279	1083	0.083	3302	54.4	212	
5 h	651	825	284	1112	0.087	3302	39.8	186	12%
25 h	671	827	292	1099	0.081	3304	27.1	159	25%
100 h	672	846	294	1133	0.084	3302	21.3	144	32%
200 h	674	837	294	1115	0.082	3299	22.7	148	30%

In-Situ SSM Testing System



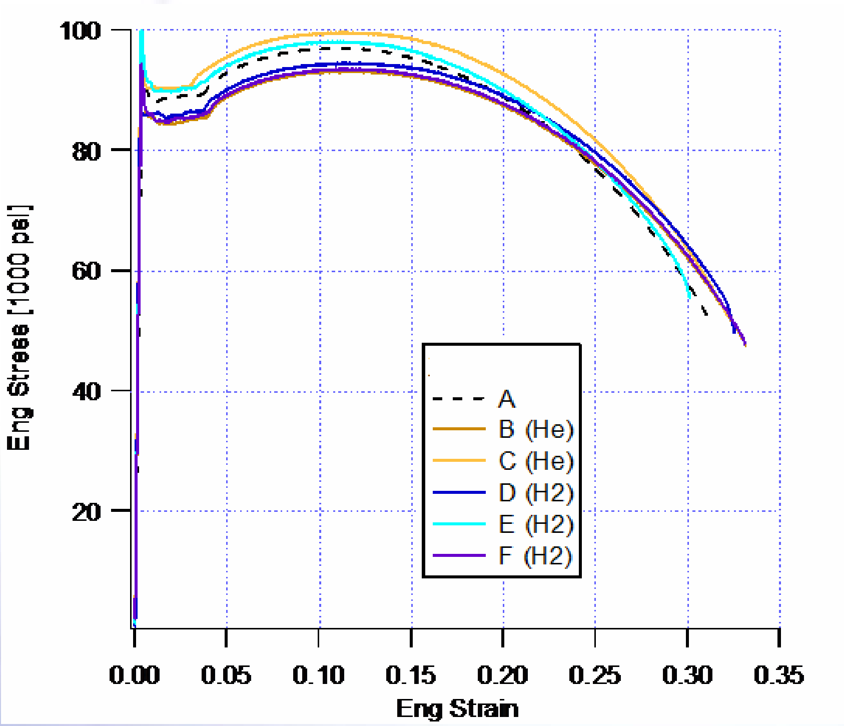
Summary of Results In-Situ Testing System

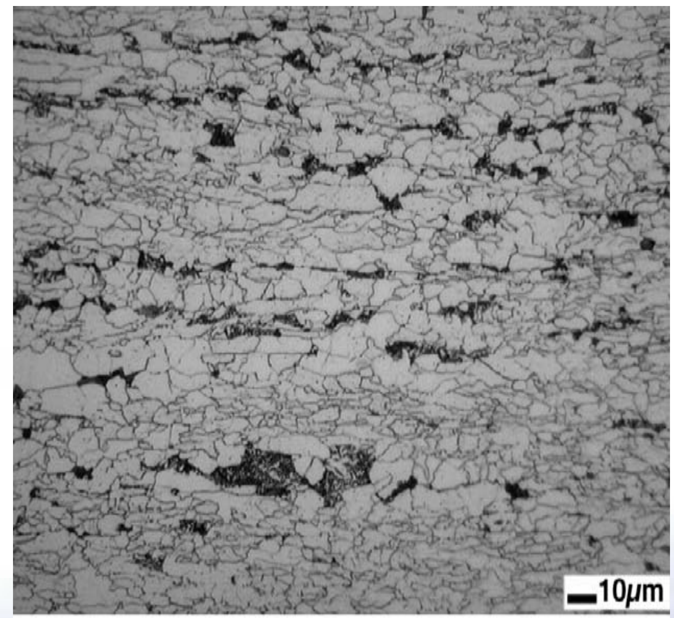
- **The ABI-determined fracture toughness of X80 pipeline steel decreased by 12.3%, 25%, 32%, and 30% after 2,000 psi hydrogen exposure times of 5, 25, 100, and 200 hours. It appears that the reduction in fracture toughness saturates at 100 h for the 9.5-mm (0.375-inch) thick sample.**
- **This compared well with the 49% reduction in fracture toughness of 0.5T CT sample tested in an autoclave by Praxair. The complete immersion in hydrogen is more severe than actual hydrogen pipeline transmission application. The ABI hydrogen chamber better simulates the real pipeline steel application. Increase in tensile properties was very small for X80 pipeline steel and no changes were measured for other grades.**
- **No reduction in fracture toughness was observed for ABI disc samples manufactured from Grades B, X52, and X70 exposed to hydrogen pressure with the X80 steel.**

Embrittlement of Steels was Evaluated using Ex-Situ Tensile Tests

- X-70 and X-80 pipeline steels were tested for hydrogen embrittlement using tensile tests after exposure to 20,000 psi hydrogen at 100^{o}C for 8 days
- To account for any temperature effects, companion set of specimens was tested after exposure to 5,000 psi helium at 100^{o}C for 8 days
- Tensile tests were conducted ex-situ in air after removing the samples from the hydrogen atmosphere
- Amount of hydrogen trapped within the sample after charging IS NOT KNOWN

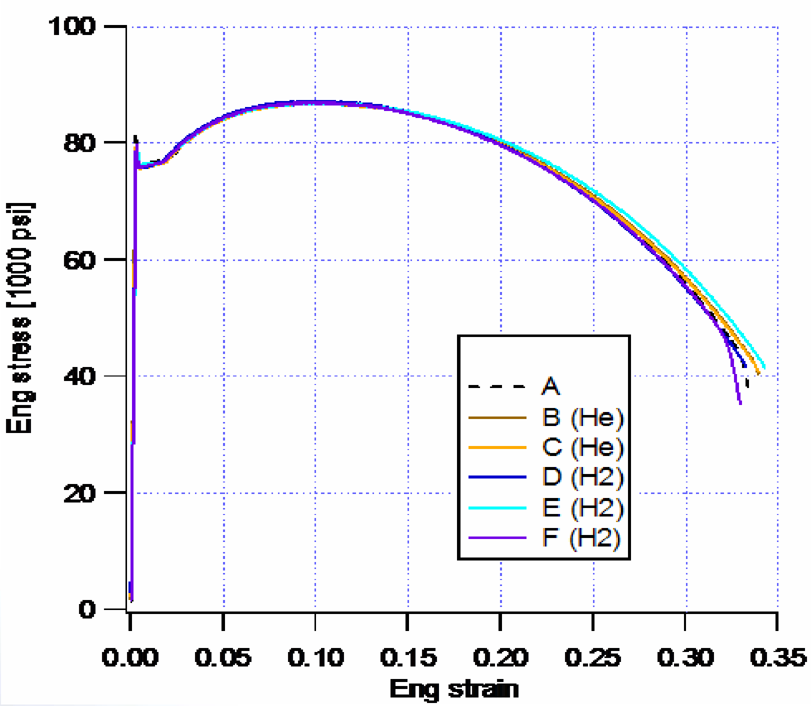
Effect of Hydrogen on the Mechanical Properties of Steel A

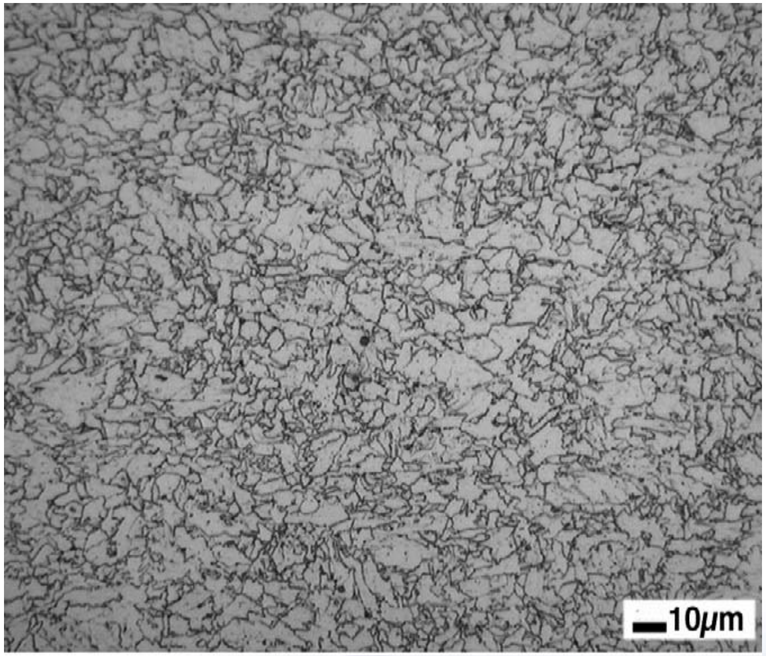




Microstructure: Ferrite + Pearlite
Yield Stress: Intermediate
Note stress- strain curves variability

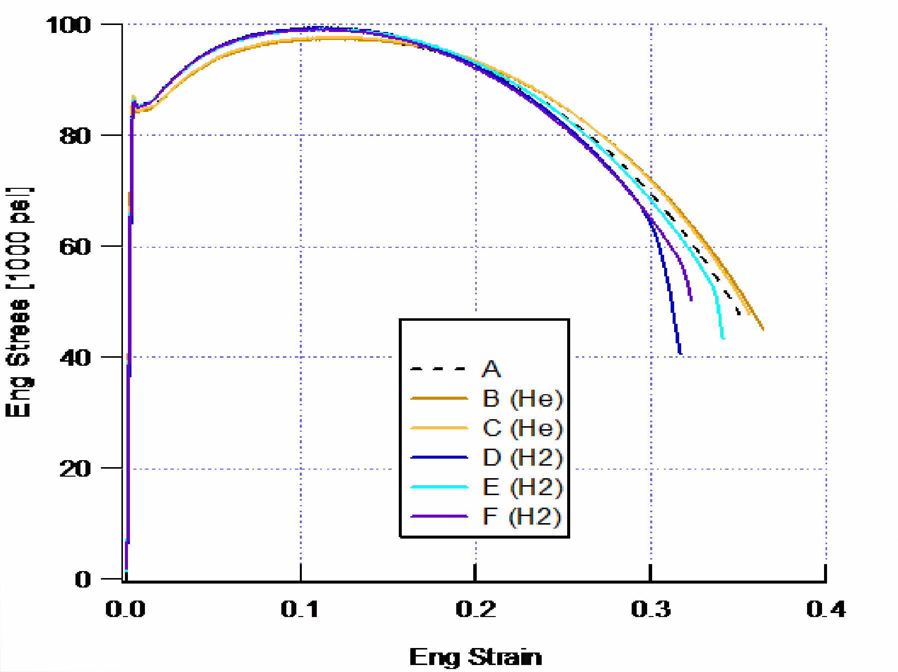
Effect of Hydrogen on the Mechanical Properties of Steel B

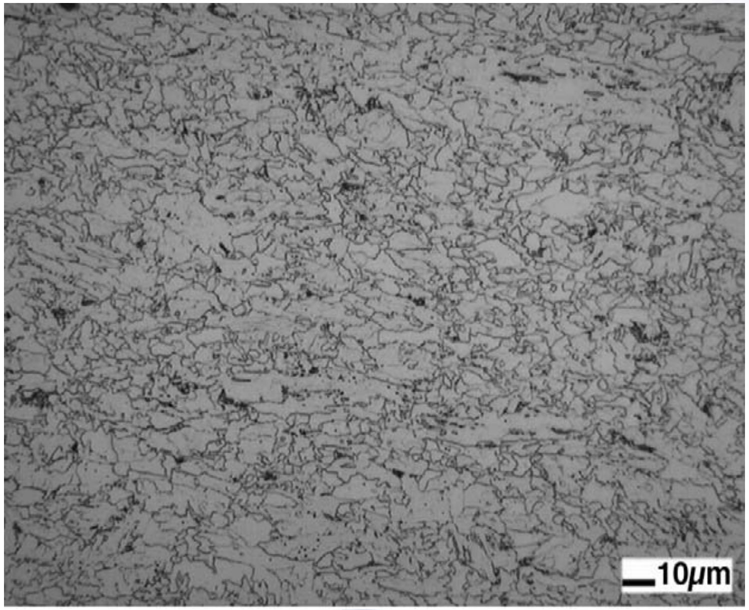




Microstructure: Ferrite + Acicular Ferrite
Yield Stress: Low
Note consistent stress-strain curves

Effect of Hydrogen on the Mechanical Properties of Steel C





Microstructure: Ferrite/acicular ferrite + small quantity pearlite
Yield Stress: High
Note stress-strain curve with slight variability

Hydrogen Embrittlement of Steels was Evaluated using Ex-Situ Tensile Tests

Material		ID	Note	Min diameter [in]	Failure strain	Tensile modulus [10^6 psi]	
X70	A	A	As is	0.1605	0.31	26.6	
		B	He	0.1605	0.33	29.2	
		C	He	0.1612	0.32	31.9	
		D	H_2	0.1608	0.32	31.4	Medium YS
		E	H_2	0.1607	0.30	29.5	
		F	H_2	0.1605	0.33	28.7	
X80	B	A	As is	0.1601	0.33	30.5	
		B	He	0.1605	0.34	33.8	Low YS
		C	He	0.1603	0.34	32.7	
		D	H_2	0.1603	0.33	29.8	
		E	H_2	0.1606	0.34	29.9	
		F	H_2	0.1605	0.33	29.6	
X80	C	A	As is	0.1609	0.35	28.9	
		B	He	0.1607	0.36	31.3	High YS
		C	He	0.1602	0.36	30.4	
		D	H_2	0.1601	0.32	28	
		E	H_2	0.1602	0.34	29.5	
		F	H_2	0.1603	0.32	29.8	

Recent Testing Of Stainless Steels with Differing Alloy Content

Table 1. Compositions (wt%) of the type 316 stainless steels used in this study.

ID	alloy	Fe	Cr	Ni	Mn	Mo	N	C	Si	S	P	M_{D30} (°C)
A	316	Bal	17.72	12.13	1.69	2.36	0.03	0.041	0.57	0.027	0.026	-40
B	316L	Bal	17.7	13.5	0.31	2.63	0.01	0.017	0.35	0.006	0.011	-25
C	316/316L	Bal	16.63	11.07	1.29	2.02	0.023	0.03	0.49	0.024	0.03	+3
D	316	Bal	17.60	12.13	1.68	2.36	0.04	0.043	0.56	0.024	0.024	-44
E	316L	Bal	17.55	13.25	1.16	2.70	0.04	0.022	0.63	0.006	0.015	-47

Tensile Properties of Stainless Steels

Table 2. Tensile properties of type 316 stainless steels in the annealed and strain-hardened condition for materials without hydrogen (non-charged) and with internal hydrogen (precharged).

Alloy	Condition	Condition	S_y (MPa)	S_u (MPa)	RA (%)	El_u (%)	El_t (%)
A 316	Annealed	non-charged	257	602	80	54	67
		precharged	311	651	69	55	66
	Strain-hardened	non-charged	563	735	78	26	47
		precharged	665	811	66	25	45
B 316L	Annealed	non-charged	221	551	85	57	71
		precharged	279	607	72	60	71
	Strain-hardened	non-charged	594	736	78	20	41
		precharged	690	812	68	21	40
C 316/316L	Annealed	non-charged	253	585	81	58	70
		precharged	306	642	62	57	66
	Strain-hardened	non-charged	583	722	78	24	45
		precharged	694	819	59	23	41
D 316	Annealed	non-charged	243	579	85	51	68
		precharged	310	636	70	62	73
	Strain-hardened	non-charged	693	784	77	9	37
		precharged	763	859	58	15	36
E 316L	Annealed	non-charged	242	585	83	56	71
		precharged	301	631	72	59	71
	Strain-hardened	non-charged	790	863	77	2	29
		precharged	850	926	70	7	32

Engineering Stress Strain

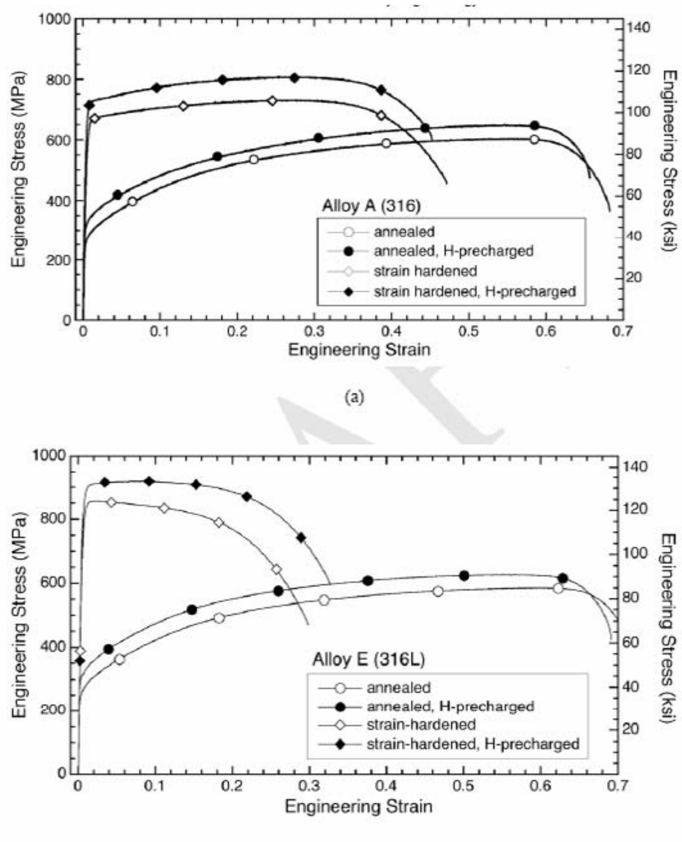


Figure 2. Tensile flow curves of both annealed and strain-hardened microstructures in the non-charged and hydrogen-precharged conditions: (a) alloy A and (b) alloy E.

Ductility as a Function of Nickel Composition

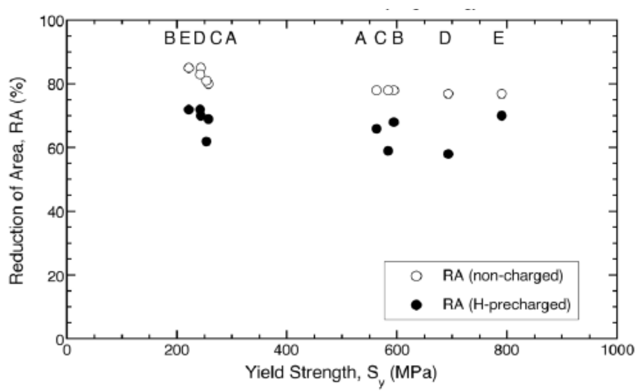


Figure 4. Ductility as a function of yield strength of the five alloys in the annealed and strain-hardened conditions; alloys are designated on the plot by letter.

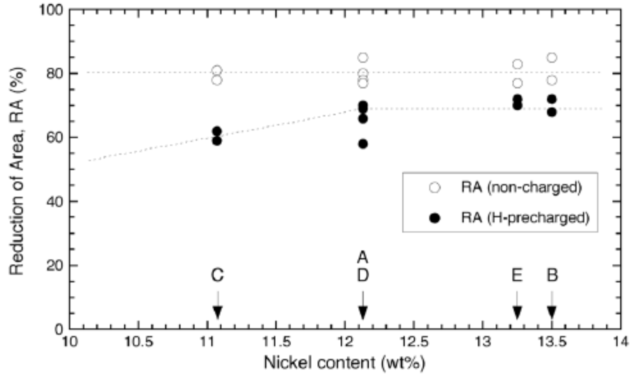


Figure 5. Ductility as a function of nickel composition for the five alloys in both annealed and strain-hardened conditions; alloys are designated on the plot by letter.

Equilibrium Hydrogen Content

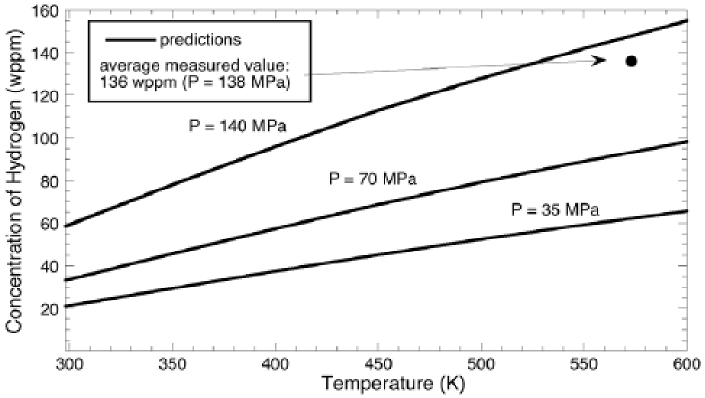
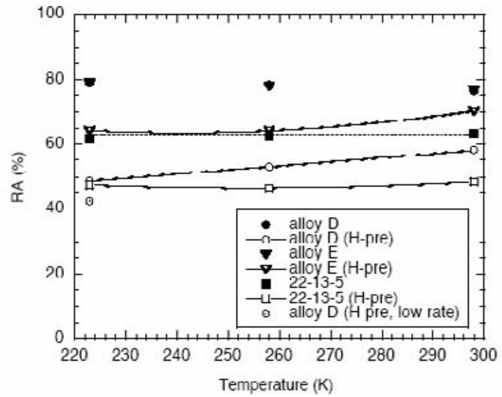


Figure 8. Equilibrium hydrogen content predictions for type 300-series stainless steels from Ref. [21] and the average hydrogen content for the type 316 stainless steels measured in this study.

Temperature Sensitivity



alloy D = 316
alloy E = 316L (higher nickel)

note: closed circles and closed triangles are essentially superimposed (ie the same)

strain rate - $1.5 \times 10^{-3}\ s^{-1}$
"low rate" strain rate - $5 \times 10^{-5}\ s^{-1}$

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