Technical Reference on Hydrogen Compatibility of Materials

High-Alloy Ferritic Steels:
Martensitic Stainless Steels
Heat Treatable (Fe-Cr type) (code 1820)

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1. General

The martensitic stainless steels with low nickel are hardenable by heat treatment to a range of mechanical properties. These alloys are used for their combination of high strength and corrosion resistance [1]. The heat treatment process used to attain high strength in the Fe-Cr type stainless steels involves quenching and tempering.

In general, very little data exists for these alloys in gaseous hydrogen; however, the available data indicate that martensitic stainless steels are susceptible to hydrogen-assisted fracture in gaseous hydrogen, a characteristic common to high-strength alloys. The data from notched tensile tests indicate that this class of alloys is extremely susceptible to fracture in hydrogen environments. Indeed, the Fe-Cr martensitic stainless steels are among the families of alloys that are most susceptible to hydrogen-assisted fracture. Based on the available data, these alloys must be used with caution as structural materials in hydrogen gas service.

1.1 Composition and microstructure

The Fe-Cr martensitic stainless steels are distinguished from the precipitation-hardening, martensitic stainless steels by the lack of nickel as an alloying constituent. The Fe-Cr martensitic stainless steels fall into two categories: low carbon and high carbon. Table 1.1.1 lists the approximate composition specification ranges for several common Fe-Cr martensitic stainless steels. Table 1.1.2 provides the compositions of several heats of martensitic stainless steels used to study the effects of hydrogen on mechanical properties.

1.2 Common designations

The Fe-Cr martensitic stainless steels are typically referred to by their AISI designation: type 400-series alloys. The 400-series also consist of a number of non-hardenable varieties, commonly referred to as the ferritic stainless steels (which are not included in this section). There are also a group of similar alloys developed specifically for fusion reactor applications, such as MANET; these are not included.

2. Permeability, Diffusivity and Solubility

We are unaware of any permeation measurements for this class of materials exposed to gaseous hydrogen. Based on electrochemical measurements of effective diffusivity in the precipitation-hardening, martensitic stainless steels, we might expect hydrogren diffusivity to be intermediate between low-alloy steels and austenitic stainless steels: on the order of 10^{-12} m^2/s.

3. Mechanical Properties: Effects of Gaseous Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

The data in Table 3.1.1.1 show that the ductility of type 410 and type 440C alloys is significantly degraded when tested in high-pressure hydrogen. Hydrogen-precharged type 440C in a low-strength condition also experiences reduced elongation at both room temperature and low temperature (200 K) [2].

3.1.2 Notched tensile properties

The data in Table 3.1.2.1 show that the notched tensile strength of type 410 and type 440C martensitic stainless steels is extremely degraded when tested in high-pressure hydrogen. It has also been shown that partial pressures of hydrogen less than an atmosphere can significantly reduce the notched tensile strength of type 410 [3].

3.2 Fracture mechanics

No known published data in hydrogen gas.

3.3 Fatigue

No known published data in hydrogen gas.

3.4 Creep

No known published data in hydrogen gas.

3.5 Impact

No known published data in hydrogen gas.

3.6 Disk rupture testing

Disk rupture tests show that type 410 stainless steel is extremely sensitive to fracture in hydrogen gas [4].

4. Fabrication

The Fe-Cr martensitic stainless steels are available in a range of product forms and a variety of compositions; however, the limited evidence suggests that 400-series alloys are generally susceptible to hydrogen-assisted fracture.

5. References

1. RA Lula. Stainless Steel (revised from "An Introduction to Stainless Steel" by JG Parr and A Hanson). Metals Park OH: American Society for Metals (1986).
2. GR Caskey. Hydrogen Compatibility Handbook for Stainless Steels (DP-1643). EI du Pont Nemours, Savannah River Laboratory, Aiken SC (June 1983).

3. RJ Walter and WT Chandler. Effects of High-Pressure Hydrogen on Metals at Ambient Temperature: Final Report. Rocketdyne (report no. R-7780-1) for the National Aeronautics and Space Administration, Canoga Park CA (February 1969).
4. J-P Fidelle, R Bernardi, R Broudeur, C Roux and M Rapin. Disk Pressure Testing of Hydrogen Environment Embrittlement. in: Hydrogen Embrittlement Testing, ASTM STP 543, American Society for Testing and Materials. (1974) p. 221-253.
5. ASTM DS-56H, Metals and Alloys in the UNIFIED NUMBERING SYSTEM (SAE HS-1086 OCT01). American Society for Testing and Materials (Society of Automotive Engineers) (2001).
6. RP Jewitt, RJ Walter, WT Chandler and RP Frohmberg. Hydrogen Environment Embrittlement of Metals. Rocketdyne for the National Aeronautics and Space Administration, Canoga Park CA (March 1973).

Table 1.1.1. Compositions (wt%) of several Fe-Cr martensitic stainless steels [5].

UNS no.	AISI no. / common name	Fe	Cr	Mn	Si	C	Other
S41000	410	Bal	11.50 13.50	1.00 max	1.00 max	0.15 max	0.040 max P; 0.030 max S
S42000	420	Bal	12.00 14.00	1.00 max	1.00 max	>0.15	0.040 max P; 0.030 max S
S44004	440C	Bal	16.00 18.00	1.00 max	1.00 max	0.95 1.20	0.75 max Mo; 0.040 max P; 0.030 max S

Table 1.1.2. Compositions (wt%) of several heats of Fe-Cr martensitic stainless steels used to study hydrogen effects on mechanical properties.

Heat	Alloy	Fe	Cr	Mn	Si	C	Other	Ref.
W69-410	410	Bal	12.26	0.71	0.60	0.145	0.016 P; 0.007 S; 0.40 Ni; 0.08 Mo; 0.11 Cu; 0.02 Al	[3]
W69-440C	440C	Bal	17.33	0.48	0.33	0.96	0.013 P; 0.024 S; 0.36 Ni; 0.48 Mo	[3]

Table 3.1.1.1. Smooth tensile properties of martensitic stainless steels at room temperature; measured with internal hydrogen or in external hydrogen gas.

Material	Thermal precharging	Test environment	Strain rate (s^{-1})	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)	Ref.
410 (heat W69-410)	None	air	0.67 x10^{-3}	1324	1524	—	15	60	[3, 6]
	None	69 MPa H_2		—	1144	—	1.3	12	
440C (heat W69-440C)	None	air	0.67 x10^{-3}	1627	2075	—	3.5	3.1	[3, 6]
	None	69 MPa H_2		—	820	—	—	0	
440C	None	air	—	377	620	—	7.1	—	[2]
	(1)	air		377	575	—	4.6	—	
	None	air, 200 K		406	670	—	7.7	—	
	(1)	air, 200 K		450	570	—	4.2	—	

(1) 69 MPa deuterium, 620 K, 500 h (gauge diameter ~ 5 mm)

Table 3.1.2.1. Notched tensile properties of martensitic stainless steels at room temperature; measured in external hydrogen gas.

Material	Specimen	Thermal precharging	Test environment	Displ. rate (mm/s)	S_y † (MPa)	σ_s (MPa)	RA (%)	Ref.
410 (heat W69-410)	(a)	None	air	~0.35 x10^{-3}	1324	2730	1.4	[3, 6]
		None	69 MPa H_2		—	565	0.6	
440C (heat W69-440C)	(a)	None	air	~0.35 x10^{-3}	1627	1027	0.6	[3, 6]
		None	69 MPa H_2		—	510	0	

† yield strength of smooth tensile specimen

(a) V-notched specimen: 60° included angle; minimum diameter = 3.81 mm; maximum diameter = 7.77 mm; notch root radius = 0.024 mm. Stress concentration factor (K_t) = 8.4.