# Technical Reference on Hydrogen Compatibility of Materials

## High-Alloy Ferritic Steels:
## Martensitic Stainless Steels
## Precipitation Hardening (Fe-Cr-Ni type) (code 1810)

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### 1. General

The Fe-Cr-Ni martensitic stainless steels are precipitation-strengthened alloys that can be heat treated to a range of mechanical properties. These alloys are used for their combination of high strength, high toughness, and corrosion resistance, as well as their ability to maintain strength to somewhat elevated temperature (up to about 573 K). However, martensitic stainless steels suffer a loss in toughness at low (subzero) temperature. Additional details are available in standard references on stainless steels (e.g., Refs. [1, 2]), and from manufacturers' data sheets.

The available data indicate that Fe-Cr-Ni, precipitation-strengthened martensitic stainless steels are very sensitive to hydrogen-assisted fracture, a common characteristic of high-strength alloys, and this degradation of properties increases with increasing strength of the material. Solution annealed materials appear to be much less sensitive to hydrogen-assisted fracture, although no tests have been performed in high-pressure hydrogen gas. In general, very little data exist for these alloys in gaseous hydrogen, thus a few representative reports are cited here that present data from tests performed with electrolytic precharging.

Based on the available data, this family of alloys is not recommended for service in hydrogen environments.

### 1.1 Composition and microstructure

The Fe-Cr-Ni martensitic stainless steels have lower nickel contents than the semi-austenitic stainless steels with additions of alloying agents not generally associated with the (non-precipitation strengthened) austenitic alloys, such as aluminum, copper, niobium and titanium. Table 1.1.1 lists the compositional specification ranges for several common Fe-Cr-Ni martensitic stainless steels.

### 1.2 Common designations

Tradenames are commonly used for these alloys. Some of the common alloys are referred to by the chromium and nickel content, such as 17-4 PH (AISI type 630) and 15-5 PH (ASTM XM-12), the designation "PH" indicates its status as a precipitation-hardening composition. The Custom 4xx alloys represent another family of tradenames from this class of alloys. Stainless W (AISI type 635) is common precipitation-strengthened martensitic stainless steel.

### 2. Permeability, Diffusivity and Solubility

We are unaware of any permeation and diffusion measurements for this class of materials exposed to gaseous hydrogen; however, hydrogen diffusion has been measured by electrochemical methods. The effective diffusivity is given in Table 2.1 as determined from several electrochemical studies. The effective hydrogen diffusivity in these materials is several orders of magnitude greater than the austenitic stainless steels.

## 3. Mechanical Properties: Effects of Gaseous Hydrogen

### 3.1 Tensile properties

#### 3.1.1 Smooth tensile properties

Hydrogen precharging of 17-4 PH in 13.8 MPa hydrogen gas at 475 K for 24 hours resulted in significant loss of reduction of area for smooth tensile specimens tested in air for the solution annealed (SA) and precipitation-strengthened (H900) conditions [3].

In addition, there are data from electrochemically precharged materials for a variety of alloys from this family. These studies indicate modest changes in properties in the solution annealed condition [4, 5], and significant degradation of strength and ductility in the precipitation-strengthened conditions [3-6].

#### 3.1.2 Notched tensile properties

The notched tensile strength of solution-annealed and precipitation-hardened 17-4 PH was not affected by testing in 2 atmospheres of hydrogen gas [7]. However, evaluation of the fracture surfaces indicated a change in fracture mode [7], which suggests that notched tensile strength may not be an adequate metric for hydrogen-assisted fracture at lower gas pressures. The notched tensile strength is likely degraded in high fugacity hydrogen.

### 3.2 Fracture mechanics

The fracture toughness of 17-4PH martensitic stainless steel is substantially reduced when tested in hydrogen gas, Table 3.2.1. The fracture toughness is reduced by more than 50% for the solution-annealed condition in 69 MPa hydrogen gas, and this reduction increases with strength to almost 90% for the peak-aged condition [8]. These data also show that the susceptibility to hydrogen-assisted fracture increases with gas pressure.

### 3.3 Fatigue

Crack growth rates in 17-4 PH were significantly increased in 2 atmospheres of hydrogen gas [9]. Fracture surfaces from these fatigue specimens show less plasticity in the fracture process compared to tests in air.

### 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 martensitic stainless steels (such as 17-4PH and PH13-8Mo) are extremely sensitive to hydrogen-assisted fracture in gaseous environments [10].

## 4. Fabrication

Precipitation-hardening martensitic stainless steels have considerable variation in alloy composition and are available in a range of product forms; nevertheless, the limited data suggest that this class of stainless steels is very susceptible to hydrogen-assisted fracture both prior to and after aging.

### 4.1 Primary processing

Forming and machining operations are generally performed in the solution-annealed (SA) condition, which disrupts the oxide that forms during solution annealing in air. It has been suggested in the literature that solution-annealing finished parts of 17-4 PH prior to precipitation hardening results in a uniform oxide that prevents hydrogen uptake during electrochemical precharging [3]. This study also proposes extended precipitation-strengthening heat treatments in oxygen to achieve a robust and continuous oxide. The kinetics of hydrogen transport through the oxides on these alloys has not been reported.

### 4.2 Heat treatment

The material is typically distributed in the solution annealed condition (SA) and heat treated to the desired properties. Heat treatments are most commonly designated by the letter “H” and temperature in degrees Fahrenheit, such that H900 indicates precipitation strengthening at 900˚F (755 K).

### 4.3 Properties of welds

The martensitic stainless steels are readily weldable with filler wire that matches the base material, although austenitic stainless steel (300-series) filler wire can be used to produce joints with lower strength then the base material [1].

## 5. References

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8. GR Caskey. Hydrogen Compatibility Handbook for Stainless Steels (DP-1643). EI du Pont Nemours, Savannah River Laboratory, Aiken SC (June 1983).
9. LW Tsay, TY Yang and MC Young. Embrittlement of laser surface-annealed 17-4 PH stainless steel. Mater Sci Eng A311 (2001) 64-73.
10. J-P Fidelle. Present status of the disk pressure test for hydrogen embrittlement. in: L Raymond, editor. Test Methods for Hydrogen Embrittlement: Prevention and Control, ASTM STP 962, American Society for Testing and Materials. (1988) p. 153-172.
11. 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).

Table 1.1.1. Compositions (wt%) of several common commercial precipitation-strengthened martensitic stainless steels of the Fe-Cr-Ni type [11].

| UNS No | Common Name (AISI/ASTM) | Fe | Cr | Ni | Mo | Cu | Al | Nb | Ti | Mn | Si | C | other |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S17400 | 17-4 PH (Type 630) | Bal | 15.0 17.5 | 3.00 5.00 | — | 3.00 5.00 | — | 0.15 0.45 | — | 1.00 max | 1.00 max | 0.07 Max | 0.040 max P; 0.030 max S |
| S15500 | 15-5 PH (XM-12) | Bal | 14.00 15.50 | 3.50 5.50 | — | 2.50 4.50 | — | 0.15 0.45 | — | 1.00 max | 1.0 max | 0.07 max | 0.040 max P; 0.030 max S |
| S13800 | PH 13-8 Mo (XM-13) | Bal | 12.25 13.25 | 7.50 8.50 | 2.00 2.50 | — | 0.90 1.35 | — | — | 0.20 max | 0.10 max | 0.05 max | 0.01 max N; 0.01 max P; 0.008 max S |
| S45500 | Custom 455 (XM-16) | Bal | 11.00 12.50 | 7.50 9.50 | 0.50 max | 1.50 2.50 | — | 0.10 0.50 | 0.80 1.40 | 0.50 max | 0.50 max | 0.05 max | 0.040 max P; 0.030 max S |

Table 2.1. Hydrogen diffusivity in precipitation-strengthened martensitic stainless steels (Fe-Cr-Ni type) at room temperature.

| Material | Condition‡ | Method | Diffusivity ($m^2/s$) | Ref. |
|---|---|---|---|---|
| 17-4 PH | SA | Electrochemical | $0.46 \times 10^{-12}$† | [5] |
| | H900 | | $0.28 \times 10^{-12}$† | |
| 17-4 PH | SA | Electrochemical | $2.74 \times 10^{-12}$† | [7] |
| | H900 | | $0.97 \times 10^{-12}$† | |
| | H1025 | | $0.81 \times 10^{-12}$† | |

‡ SA = solution annealed; H900 = aged at 755 K; H1050 = aged at 839 K
† effective diffusivity ($D_{eff}$)

Table 3.2.1. Fracture toughness of precipitation-strengthened martensitic stainless steels (Fe-Cr-Ni type) at room temperature; measured in external hydrogen gas.

| Material | Test method | Thermal precharging | Test environment | $S_y$ (MPa) | $K_Q$ ‡ (MPa) | Ref. |
|---|---|---|---|---|---|---|
| 17-4PH SA | C-specimen | None | 69 MPa He | ( 28 )† | 97 | [8] |
| | | None | 3.5 MPa $H_2$ | | 71 | |
| | | None | 69 MPa $H_2$ | | 31 | |
| 17-4PH H817 | C-specimen | None | 69 MPa He | ( 38 )† | 104 | [8] |
| | | None | 3.5 MPa $H_2$ | | 31 | |
| | | None | 69 MPa $H_2$ | | 20 | |
| 17-4PH H950 | C-specimen | None | 69 MPa He | ( 42 )† | 97 | [8] |
| | | None | 3.5 MPa $H_2$ | | 29 | |
| | | None | 69 MPa $H_2$ | | 13 | |
| 17-4PH H1100 | C-specimen | None | 69 MPa He | ( 35 )† | — | [8] |
| | | None | 3.5 MPa $H_2$ | | 57 | |
| | | None | 69 MPa $H_2$ | | 34 | |

SA = solution annealed (1339 K, 2 h); H817 = underaged (SA + 719 K, 1h); H950 = peak aged (SA + 783 K, 1 h); H1100 = overaged (SA + 866 K, 1 h)
† Rockwell hardness, scale C
‡ not clear if plane strain requirements are met in these studies