RINA Consulting S.p.A.

Method Statement for Hydrogen-Ready metallic Valves

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ACRONYMS AND SYMBOLS

Al	Aluminium
ANSI	American National Standards Institute
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
B	Boron
BPVC	Boiler and Pressure Vessel Code
Cr	Chromium
EN	European Standards
GR	General Requirements
H	Hydrogen
HE	Hydrogen Embrittlement
HS	High strength
IP	Industrial Piping
ISO	International Organization for Standardization
Mo	Molybdenum
MOP	Max Operating Pressure
NACE	National Association of Corrosion Engineers
Ni	Nickel
PL	Pipelines
Ti	Titanium
TMCP	Thermomechanical Controlled Process
W	Tungsten
Zr	Zirconium

1 PURPOSE

This Method Statement provides a systematic definition of the applicable requirements to be satisfied by a manufactured carbon steel valve to be qualified as “**Hydrogen-Ready**” according to the Standard Code ASME B31.12-2019 “Hydrogen Piping and Pipelines” (Ref. [1]).

This Method Statement applies to the typologies of valves listed in Table IP-8.1.1-1 of ASME B31.12 intended for construction of gas transmission and distribution pipelines as well as hydrogen piping systems.

Where necessary, further details, in compliance with the philosophy and requirements of ASME B31.12-2019, are provided.

2 APPLICATIONS AND LIMITATIONS

This Method Statement applies to the typologies of valves listed in Table 2.1 below.

Valves manufactured in accordance with the reported standards are suitable for use in hydrogen service at intended pressure–temperature ratings provided that the material requirements reported in Sect. 3 are met.

Table 2.1: Valve reference standards.

Service condition	Reference standard	ASME B31.12 reference section
Pipelines (transport and distribution lines)	ASME B16.34 ASME B16.38 API 6D API 609 API 600 API 602	ASME B31.12 PL-2.2.2
Piping systems	ASME B16.10 ASME B16.34 MSS SP-80	ASME B31.12 IP-4.1.1 Table IP-8.1.1-1

Unlisted valves but which conform to a published specification or standard, may be used within the following limitations:

- ✓ The designer shall be satisfied that composition, mechanical properties, method of manufacture, and quality control are comparable to the corresponding characteristics of listed components.
- ✓ Pressure design shall be verified in accordance with Sect. 4 of this document.

In Table 2.2 relevant applications and limitations are reported.

Table 2.2: Applications and limitations (operating conditions).

Item	Applications and limitations	ASME B31.12 reference section
Transported gas	Hydrogen with natural gas blends with hydrogen content equal or higher than 10% (by volume) up to 100% and pure hydrogen	Para. PL-1.3 (e)
Pressure	Maximum Operating Pressure (MOP) ≤ 3000 psi (≈206 bar) (Note 1)	Para. PL-1.3 (c) Table GR-2.1.1-2 General Note (a)
Temperature	Referring to what is reported for the pipelines, design temperature in the range 232°C (450°F) and -62°C (-80°F)	Para. PL-1.3 (b)

Note 1: Referring to the pressure limits of pipelines, which represent the limiting element, despite the pressure limitations for steel grades higher than X65 (Table GR-2.1.1-2 of ASME B31.12-2019), maximum pressure has been set equal to 3000 psi (≈206 bar) for all the steel grades up to X80 based on indications coming from clause (b) of Sect. GR-2.1.1 and Table IX-5A.

3 MATERIAL REQUIREMENTS

3.1 METALLIC MATERIALS

3.1.1 Preamble

Valves consist of various components having different functions and working at different stress levels, therefore, special considerations are to be made to determine for which components specific requirements for material suitability for hydrogen service shall apply.

Moreover, depending on the specific application (transport/distribution or industrial piping system) different metallic materials can be selected. In particular, the present document considers the following classes of materials:

- ✓ Carbon steel.
- ✓ Low and intermediate alloy steels.
- ✓ High alloy ferritic steels.
- ✓ Austenitic stainless steels with greater than 7% nickel.
- ✓ Aluminium and aluminium alloys.
- ✓ Copper and Copper alloys.
- ✓ Titanium and titanium alloys.

The requirements reported in this section apply to materials in direct contact with hydrogen.

The following paragraphs provide an overview of the admitted metallic materials and relevant requirements to confirm suitability for hydrogen service from a material perspective.

3.1.2 Listed, prohibited, and unlisted materials

The following categories of materials are identified based on their suitability with hydrogen service[1]:

- ✓ Listed materials, which are considered compatible in principle with hydrogen service. Final confirmation of material suitability needs verification that the specific requirements for material properties, listed in the following paragraphs of this document, are satisfied. Listed materials are summarized in Table IX-1A of ASME B31.12.
- ✓ Prohibited materials, which are considered non-compatible with hydrogen service and therefore their use for components in direct contact with hydrogen is not allowed. Indication of prohibited materials is provided in Para. PL 2.2.2 of ASME B31.12.
- ✓ Unlisted materials, which may be used, provided they conform to a published specification covering chemistry, physical and mechanical properties, method and process of manufacture, heat treatment, and quality control, and otherwise meet the specific requirements for material properties, listed in the following paragraphs of this document. Allowable stresses shall be determined in accordance with the applicable allowable stress basis of ASME B31.12 Code or a more conservative basis.

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[1] Para. GR-2.1.1 of ASME B31.12.

Table 3.1: Material limitations.

Item	Material limitations	ASME B31.12 reference section
Metallic Materials	**Listed materials are:** ✓ Carbon steel ✓ Low and intermediate alloy steels ✓ Austenitic stainless steels with greater than 7% nickel ✓ Aluminium and aluminium alloys ✓ Copper and copper alloys **Unlisted materials:** ✓ See Par. GR-2.1.1 (b) ✓ Duplex stainless steels ✓ High alloy ferritic steels ✓ Titanium and titanium alloys **Prohibited materials are:** ✓ Gray, ductile or cast-iron cast are not permitted ✓ Nickel and nickel alloys steels (e.g., 2.25%, 3.5%, 5%, and 9% Ni) are not permitted	Para. GR-2.1.1 Table GR-2.1.1-2 Table A-2-1
Metallic materials grades	Carbon steels grades: ≤X80 or equivalent (Table GR-2.1.1-2) Other metallic materials: see Table IX-1A of ASME B31.12	Table GR-2.1.1-2 Table IX-1A
Non-Metallic materials	Non-metallic materials are out of the scope of ASME B31.12. Non-metallic materials normally in contact with hydrogen shall be verified to be acceptable in hydrogen service. Consideration shall be given to the fact that hydrogen diffuses through these materials much more easily than through metals; therefore, the suitability of materials shall be verified. Moreover, non-metallic materials shall retain their mechanical stability with respect to strength when exposed to the full range of service conditions and lifetime as specified by the manufacturer.	-

3.1.3 General requirements for material properties in hydrogen service

In the following table the additional material properties in hydrogen service are summarized according to ASME B31.12.

Guidance on the specific grade selection is reported in the Technical Guideline (Sect. 8) of this document where the following indications are specified:

- ✓ Use of use of carbon steels, alloy steels, nickel steels, and cast irons in H2 gas (Sect. 8.1).
- ✓ Use of stainless steel in H2 gas (Sect. 8.2).
- ✓ Use of copper and copper alloys in H2 gas (Sect. 8.3).
- ✓ Use of aluminium and aluminium alloys in H2 gas (Sect. 8.4).
- ✓ Use of nickel, titanium, and their alloys in H2 gas (Sect. 8.5).

Table 3.2: General requirements for material properties.

Item	Chemistry and grade selection (Note 2)	Hardness[2] [3]	Toughness additional Charpy impact tests as reported in ASME B31.12 GR-2.1 for service temperatures below	Specified minimum strength		Maximum Hardness Bolting
				Yield	Tensile	
Carbon steel	Recommend low P and S levels, CEIIW max = 0.43. (Par. 8.4 API 6D)	≤ 235 HV10	< the relevant Curve Table IX-1A and Figure GR-2.1.2-1	≤X80 or equivalent	≤X80 or equivalent	API 6D Para. 8.6
Low and intermediate alloy steels	-	≤ 235 HV10 for Cr ≤ 2% ≤ 248 HV10 for 2 ¼ % < Cr ≤ 10%	<-29°C (-59°C for grade LC1 ASTM A352)	30-50 ksi 210-345 MPa	55 -85 ksi 380-590 MPa	API 6D Para. 8.6
Austenitic stainless steels	Avoid highly metastable grades like type 301 and 302. Use chemistries with positive delta factor [4] when significant plastic strain can be present e.g., due to coldwork/forming/bending, or accidental damage. Limit delta ferrite content i.e., max 3%. (Par. 8.4 API 6D)	-	< -198°C (for some grades in Table IX-1A < -269°C)	25-35 ksi 170-240 MPa	70-77 ksi 480-530 MPa	-
Nickel and nickel alloys	Ni and Ni alloys are all highly susceptible and shall not be used for H2 gas service. ASME B31.12 lists Monel (alloy N04400). However, this is for use in liquid hydrogen service only.[5]	-	< -198°C	25-40 ksi	70-85 ksi	-
Aluminium and aluminium alloys	-	-	< -269°C	2.5-35 ksi	8.5-44 ksi	-
Copper and copper alloys	Use oxygen free or deoxidized copper alloys. Although Cu-Ni alloys are listed in ASME B31.12, they should be used with caution due to presence of Ni which may degrade HE resistance.[6]	-	< -198°C	9-40 ksi 60-275 MPa (410 MPa for HS grades)	30-90 ksi 207-620 MPa (690 MPa for HS grades)	-

Note 2: Chemistry is to comply with ASME B31.12 and API 6D minimum requirements plus the following additional prescriptions:

✓ Phosphorus (P)	max 0.015 wt%
✓ Nickel (Ni)	max 0.5 wt%

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[2] ASME B31.12 Para. GR-3.10.

[3] See also Table A.1-ISO15156.

[4] See Sect. 8.1.

[5] See Sect. 8.5.

[6] See 8.3.

3.1.4 Non-Metallic Materials

Non-metallic materials normally in contact with hydrogen shall be determined to be acceptable in hydrogen service. Consideration shall be given to the fact that hydrogen diffuses through these materials much more easily than through metals; therefore, the suitability of materials shall be verified.

Moreover, non-metallic materials shall retain their mechanical stability with respect to strength when exposed to the full range of service conditions and lifetime as specified by the manufacturer.

It should be noted that a test method for evaluating material compatibility in compressed hydrogen applications for polymers is proposed by CSA/ANSI CHMC 2:19.

4 DESIGN CRITERIA FOR UNLISTED VALVES[7]

The rules specified in this section shall be intended for pressure design of valves not covered in Table 2.1, but may be used for a special or more rigorous design of such valves, or for rating listed valves non having specific rate[8].

Pressure design of unlisted components and other piping elements shall be based on calculations in accordance with the design principles of ASME B31.12 Code. These calculations shall be substantiated by one or more of the means stated in bullet 1 through bullet 4 below, considering applicable dynamic, thermal, and cyclic effects in Paras. IP-2.1.7 through IP-2.1.8 of ASME B31.12, as well as thermal shock. Calculations and documentation showing compliance with bullet 1, 2, 3 or 4, and 5 shall be available for the owner's approval:

1. Extensive, successful service experience under comparable conditions with similarly proportioned components of the same or like material.
2. Experimental stress analysis, such as described in ASME BPVC, Section VIII, Division 2, Annex 5-F.
3. Proof test in accordance with ASME B16.9, MSS SP-97, CSA HGV 4.10, or ASME BPVC, Section VIII, Division 1, UG-101.
4. Detailed stress analysis (e.g., finite element method) with results evaluated as described in ASME BPVC, Section VIII, Division 2, Part 5. The basic allowable stress from Mandatory Appendix IX, Table IX-1A shall be used in place of the allowable stress, S, in ASME BPVC, Section VIII, Division 2, where applicable. At design temperatures in the creep range, additional considerations beyond the scope of Division 2 may be necessary.
5. For any of the means stated in (a) through (d), the design engineer may interpolate between sizes, wall thicknesses, and pressure classes, and may determine analogies among related materials.

Design shall be checked for adequacy of mechanical strength under applicable loadings enumerated in Para. IP-2.1 of ASME B31.12. Adequacy of mechanical strength may be demonstrated by methods described in CSA HGV 4.10, Fittings for Compressed Hydrogen Gas and Hydrogen Rich Gas Mixtures.[9]

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[7] ASME B31.12 Para. IP-3.8.2

[8] ASME B31.12 Para. IP-2-2-3.

[9] ASME B 31.12 Para. IP-3.1 (b)

5 FUNCTIONAL REQUIREMENTS

In addition to the requirements reported in the relevant design and construction standards (Table 2.1) the following additional requirements shall be met for hydrogen service:

Adequacy of mechanical strength under applicable loadings enumerated in Para. IP-2.1 of ASME B31.12.

Adequacy of mechanical strength may be demonstrated by methods described in CSA HGV 4.10, Fittings for Compressed Hydrogen Gas and Hydrogen Rich Gas Mixtures.

Pressure test using helium as the test medium:

- ✓ Pipeline valves purchased to API 6D requirements shall be capable of passing the pressure tests described in API 6D Annex H, para. H4, using helium as the test medium.
- ✓ Other valves shall be capable of passing the pressure tests described in API 598, using helium as the test medium.
- ✓ During helium leak tests of valves in the open position, leakage shall not exceed 1 × 10−8 mL/s when differential pressure between atmosphere and internal passages of the valves is greater than 100 kPa (14.6 psi).[10]

The following additional precautionary considerations should be considered when selecting valves for hydrogen service.[11]

- ✓ Extended bonnet valves are recommended, where necessary, to establish a temperature differential between the valve stem packing and the fluid in the piping, to avoid packing leakage and external icing or other heat flux problems. The valve should be positioned to provide this temperature differential. Consideration should be given to possible packing shrinkage in low-temperature fluid service.
- ✓ The effect of external loads on valve operability and leak tightness should be considered.
- ✓ Possible packing shrinkage in low-temperature fluid service should be considered.
- ✓ Where LH2 can be trapped (e.g., in double-seated valves) and subjected to heating and consequent expansion, means of pressure relief should be considered to avoid excessive pressure build-up.
- ✓ A bolted bonnet valve, whose bonnet is secured to the body by fewer than four bolts or by a U-bolt, shall not be used.[12]

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[10] ASME B31.12 Para. IP-4.1 and APPENDIX A Clause A-7

[11] ASME B31.12 APPENDIX A Clause A-7

[12] ASME B31.12 Para. IP-4.1.2

6 INSPECTION AND TEST PLAN

The following table reports the proposed inspection and test plan (ITP) with mark-up RINA, defining the extent of the required manufacturing surveillance and verification activities.

The level of intervention is defined according to the conventional definitions with the following meanings:

✓ **Hold Point (H)**	The Client / Contractor must not proceed with the tests until it has obtained a clearance to proceed from RINA. The Client / Contractor therefore must send well in advance an inspection notification and wait for RINA's response before proceeding.
✓ **Initial Witness (IW)**	The Client / Contractor must officially notify RINA of the beginning of the phases of inspection and testing. If no issues are detected at the early stage, the Client / Contractor may proceed with the following phases of testing and production. The Client / Contractor must be invited by the supplier to participate by sending the inspection notification well in advance.
✓ **Witness Point (W)**	RINA reserves the right to be present at the testing stage (or can give up this right), but the Client / Contractor must always invite RINA to participate, by sending the inspection notification well in advance. The Client / Contractor can proceed following its plans.
✓ **Document Review (R)**	The Client / Contractor shall make available the documentation for RINA for review.

Table 6.1: Inspection and test plan

Inspection and test	Reference document	Intervention type	Remarks
Body-bonnet-stem-bolts			
Visual and dimensional check	Manufacturer Drawings	H	
Traceability and material certificates check	Sect. 2	R	
Chemical analysis and mechanical tests	Sect. 2	R	
Dye penetrant examination (PT)	ANSI B16.34	W	ONLY STEM
Magnetic particle test (MT) – 100%	ASTM A 275	W	ONLY BODY & BONNET If not applicable, 100% PT
Welding specification and WPQR review	EN 15614 / ASME IX	W	If applicable
Welders' qualification check	EN 287 / ASME IX	R	
NDE operator qualification check	EN 473/SNT-TC-1A	R	
Bonnet-end bevels			
Magnetic particles examination (MT)	ANSI B16.34	W	If not applicable, 100% PT
Radiographic examination (RT)	ANSI B16.34	W	
Ultrasonic examination (UT)	ANSI B16.34	W	
Seat rings-ball/seat			
Chemical analysis and mechanical tests	Sect. 2	R	
Dye penetrant examination (PT)	ANSI B16.34	W	
Actuator			
Visual and dimensional check	Manufacturer Drawings	R	
Assembled valve			
Visual and dimensional check	Manufacturer Drawings	H	

Inspection and test	Reference document	Intervention type	Remarks
Functional test	Manufacturer Procedure	H	
Hydrostatic test	ANSI B16.34	H	
Tightness test	ANSI B16.34	H	
Helium proof test	Sect. 4	H	
Helium leak test	Sect. 3	H	
Painting check	EN ISO 12944	H	
Final documentation check	NA	H	

7 REFERENCES

[1] ASME B31.12-2019 Hydrogen Piping and Pipelines

[2] ASME BPVC-2021 ASME Boiler and Pressure Vessel Code, Section VIII, Rules for Construction of Pressure Vessels, Division 3 Alternative Rules for Construction of High-Pressure Vessels

[3] API 5L Line pipe specification

[4] API 579-1 / ASME FFS-1 Fitness for service assessment

[5] ASTM E1681 Standard test method for determining threshold stress intensity factor for environment - Assisted cracking of metallic materials

[6] ISO 14284 Steel and iron - Sampling and preparation of samples for the determination of chemical composition

[7] ASTM E1806 Standard Practice for Sampling Steel and Iron for Determination of Chemical composition

[8] ISO 9769 Steel and iron - Review of available methods of analysis

[9] ASTM A751 Standard test methods, practices, and terminology for chemical analysis of steel products

[10] ISO 6506 (all parts) Metallic materials - Brinell hardness test

[11] ISO 6507 (all parts) Metallic materials - Vickers hardness test

[12] ISO 6508 (all parts) Metallic materials - Rockwell hardness test

[13] ASTM A370 3) Standard test methods and definitions for mechanical testing of steel products

[14] ASTM A956 Standard test method for Leeb hardness testing of steel products

[15] ASTM A1038 Standard practice for portable hardness testing by the ultrasonic contact impedance method

[16] ASTM E110 Standard test method for indentation hardness of metallic materials by portable hardness testers

[17] ISO 15156 Materials for use in H2S-containing environments in oil and gas production - Part 1: General principles for selection of cracking-resistant materials

[18] API 6D Specification for Pipeline Valves

[19] C. San Marchi and B. Somerday, “Technical Reference for Hydrogen Compatibility of Materials”, SANDIA Report SAND2012-7321 (2012)

[20] EIGA 121/14 “Hydrogen Pipeline Systems”

[21] H. Barthelemy, “Compatibility of metallic materials with hydrogen: Review of the present knowledge”, ICHS Conf. (2007), paper No. 1.4.66

[22] ASME report STP-PT-006 “Design guidelines for Hydrogen Piping and Pipelines”, (2007)

[23] NASA document “Safety Standard for Hydrogen and Hydrogen Systems”, (1997)

[24] SAE J2579: “Surface Vehicle Standard: Standard for fuel systems in fuel cell and other hydrogen vehicles”, (2018)

[25] S. Wai, R. Chidambaram, J. Richert and J. Perdomo, “Hydrogen embrittlement of SS316L instrument tubing in a hydroprocessing unit”, NACE 2020 Corrosion Conference, Paper No., C2020-14357

[26] E. Tal-Gutelmacher and D. Eliezer, “The hydrogen embrittlement of titanium-based alloys”, JOM, 57, (2005), pp. 46-49

[27]	ISO 15156-3:2015	“Petroleum and natural gas industries- Materials for use in H2S-containing environments in oil and gas production- Part 3: Cracking resistant CRAs (corrosion resistant alloys) and other alloys”
[28]	API RP 571:2011	“Damage Mechanisms Affecting Fixed Equipment in the Refinery Industry”, Second Edition

[29] Titanium Metals Corporation Publication “Corrosion resistance of titanium”, (1997)

8 TECHNICAL GUIDELINE FOR MATERIAL SELECTION

8.1 USE OF CARBON STEELS, ALLOY STEELS, NICKEL STEELS, AND CAST IRONS IN H2 GAS

Definitions

Steels are alloys of iron and carbon where the carbon content is below around 1.5 wt%. Most structural steels have carbon contents below 0.4 wt%. Steels possess a body centred cubic (BCC) crystal structure at room temperature in most cases.

In previous sections steel were referred to simply as “carbon steels”, to distinguish better from stainless steels. In this section carbon steel intends a specific kind of steel as explained below.

The main types of engineering steels are defined below:

- ✓ **Carbon steels** are steels with no minimum content specified for Al, B, Cr, Co, Mo, Ni, Nb, Ti, V, Zr, W or other element added to obtain an alloying effect. When specified Cu minimum is up to 0.40wt%. When specified, maximum level does not exceed Cu =0.60 wt%, Mn =1.65 wt%, Si = 0.6 wt% (Ref. [1]).
- ✓ **Micro alloyed steels** are those with deliberate addition of at least one of Nb, V, Ti. Note that Cr, Mo, Ni may also be present in small amounts, typically maximum is 0.5 wt%.
- ✓ **Alloy steels** are with deliberate addition of one or more alloying elements to achieve desired properties i.e., addition at least one of Cr, Mo, Ni.
- ✓ **Nickel steels** are those with deliberate high addition of Ni (Ni at least 1 wt% or more). Common grades are 2.25 Ni steels, 3.5 Ni steels, 5.5 Ni steels, 9 Ni steels.

Note that in some standards no distinction is made between carbon steels and micro alloyed steels i.e., both are referred to simply as carbon steels e.g., in ASME B31.12.

Cast irons are alloys of iron and carbon where the carbon content is typically between 2 and 4 wt%. Moreover, the impurity levels are much higher than in steels. Like steels, cast irons mostly possess a BCC crystal structure at room temperature.

The main types of cast irons are defined below:

- ✓ **Grey cast iron** contains flakes of graphite (carbon) in the structure. The name grey comes from the colour of the fracture surface after breaking (grey along the flakes).
- ✓ **White cast iron**. In this type, the carbon is in the form of Fe carbides with little or no graphite. On fracturing the surface appears white.
- ✓ **Malleable iron**. In this type a heat treatment is applied to white cast iron to allow graphite to form, making the material more malleable (easier to beat or hammer to shape).
- ✓ **Ductile cast iron**. Mg addition promotes graphite with a spheroidal shape, improving the materials ductility.

Finally, it should be noted that pure iron is not listed as a cast iron. Pure iron contains almost no carbon and is not used in structural applications due to the very low strength.

Overview of steels compatibility with H2 gas

The performance of steel grades in H2 gas varies widely and depends on many factors including strength level, hardness, and chemistry.

Figure 8.1 below showed an example of real data generated from round bar tensile tests in hydrogen gas comparing carbon steels of different strength levels. Note that the resistance to hydrogen embrittlement is expressed as a ductility ratio. This intends the reduction of cross section (at failure) in hydrogen divided by that in air. Thus, a value of 1.0 signifies no loss of ductility.

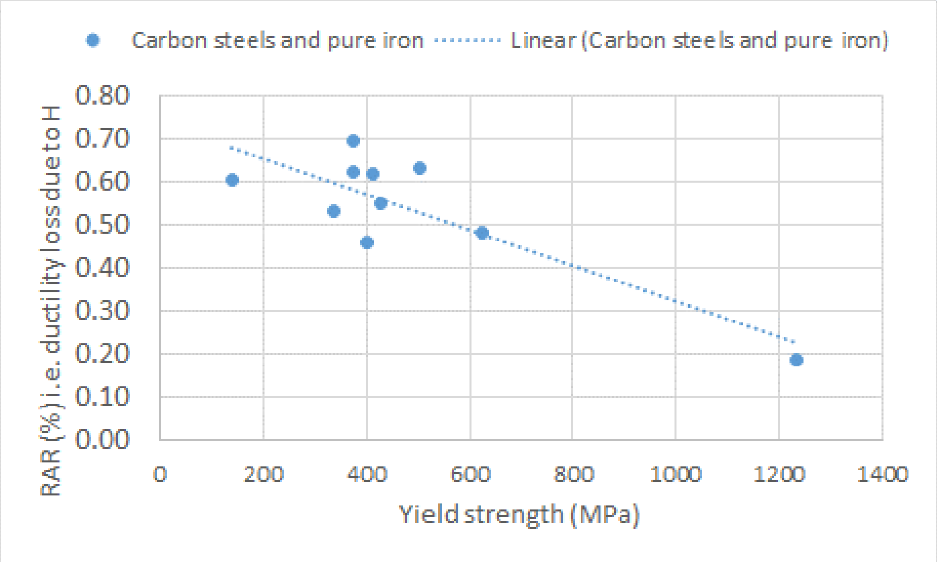


Figure 8.1: Resistance of carbon steels and pure iron (left-most data point) to hydrogen embrittlement in H2 gas at pressures of 69 and 690 bar at room temperature (Ref. [19]).

As can be seen from Figure 8.1, as strength level increases, the resistance to cracking in H2 gas is decreased. For this reason, the main standards or guidelines impose limits on the maximum strength level (Refs. [1] and [20]) or use a strength/grade dependent usage factor (maximum allowable stress) [1]. Such limits are born of experience of successful service of specific steel grades in hydrogen gas under well-defined stress levels e.g., from specific operating pressures.

Regarding steel chemistry it is known that nickel additions reduce resistance to hydrogen embrittlement (Refs. [1] and [23]). For this reason, the maximum Ni level for steels is limited to 0.5 wt% in AMSE B31.12. Moreover, so-called nickel steels i.e., those containing 1wt% Ni or more, used for low temperature applications, are not permitted for hydrogen gas service (Refs. [1] and [23]).

For impurity elements P and S, it is recommended to keep these elements to low levels to improve intrinsic toughness (improve the baseline properties). For example, for modern pipeline steels (e.g., to API PSL2), keeping the maximum P level to 0.025 wt% and maximum S level to 0.015 wt% has been recommended to obtain improved toughness (Ref. [1]). Furthermore, most (non H2) specifications for steel components or piping define maximum S and P levels no higher than 0.03 wt% each.

Recommendations on carbon equivalent have also been made (Refs. [1] and [20]). This parameter is a measure of a steels' weldability. Different formulae exist for this parameter. The most common is the CE_{IIW} carbon equivalent ($CE_{IIW} = C + \frac{Mn}{6} + \frac{Cr+Mo+V}{5} + \frac{Ni+Cu}{15}$). Limiting the carbon equivalent reduces the risk of forming hard zones and weld cracking just after welding operations. Thus, it is generally recommended to keep CEIIW not more than a value of 0.43 wt% (Ref. [1]). This limit is also a benefit for resistance to hydrogen embrittlement since such hard zones would be a potential site of weakness where hydrogen would concentrate and potentially initiate cracking.

Considering hardness, this parameter is related to the steel composition and final heat treatment. Steels parts with high hardness or locally high hardness (e.g., at welds) are more vulnerable to hydrogen embrittlement. For this reason, standards and guidelines for steels used in hydrogen service impose maximum steel hardness values. Thus EIGA 121/14 suggests a limit of 250HV10 hardness for pipeline steels and associated welds (Ref. [20]). The ASME B31.12 standard imposes a limit of 200-241HV10 for industrial piping steels (weld metal and heat affected zone) (Ref. [1]). The range of hardness values given reflects different limits for carbon and alloy steels.

Regarding heat treatment of steel components, it is also recommended to achieve a uniform and fine microstructure for best resistance to hydrogen embrittlement. Thus normalized, quenched, and tempered, or thermomechanical controlled process (TMCP), treatments are recommended for hydrogen gas service (Ref. [20]).

Concerning cast irons, it is recommended not to use any type for hydrogen gas service (Refs. [1] and [23]). Cast irons have a very low toughness compared to steels and possess a relatively low resistance to mechanical and thermal shocks (Ref. [1]). Thus, these materials are expected to be very sensitive to hydrogen embrittlement.

Finally, it is worth mentioning that steels suffer from low temperature embrittlement (become brittle at low temperatures), independently of any contact with hydrogen gas. Thus, selection of steel components for a specific application should obviously consider the design temperature, carrying out toughness tests as required by the relevant standards or material grade specifications e.g., ASME B31.12.

Material selection table for steels and cast irons in H2 gas

Table 8.1 below shows the materials selection table for steels and cast irons. The table shows the resistance of each group of metals/alloys to hydrogen embrittlement. The table shall be read taking into consideration the detailed notes under the table.

Table 8.1: Materials selection table for steels and cast irons in dry H2 gas service.

Metal/alloy	H2 compatible	H2 compatible but not recommended	Not H2 compatible	Remarks
Carbon steels + Micro alloyed steels	Refs. [1], [20], [22], and [23]			Recommend low P and S levels, CEIIW max = 0.43. Respect HV limit given in ASME B31.12. Use grades listed in ASME B31.12.
Alloy steels		Ref. [1],		Caution required for use due to higher weld hardness and alloy strength. Respect HV10 limits in ASME B31.12.
Nickel Steels			Refs. [1] and [23]	Ni steels common use for cryogenic applications. However, Ni presence causes Hydrogen embrittlement.
Grey, White, Malleable, Ductile or any other type of cast iron			Refs. [1] and [23]	Due to low toughness and sensitivity to thermal + mechanical shock these materials not compatible.

Notes

a. The table is valid only for dry H2 gas service. Tables shall not be used for conditions where water condensation occurs (Ref. [1]).

b. The table is not valid for when H2 is mixed with gases that may promote hydrogen embrittlement e.g., with H2S or CO2 or H2O.

c. The maximum H2 pressure allowed for compatible steels is 414 bar unless otherwise noted (Ref. [1]). Maximum 310 bar for carbon steels supplied to ASTM A537 or equivalent. Maximum 310 bar for alloy steels supplied to ASTM A387 or equivalent (Ref. [1]).

d. Note that the maximum H2 pressures given may be exceeded if the material is qualified by suitable testing in H2 gas (Ref. [1]).

e. The above table is valid to a maximum design temperature of 150°C. Above this temperature other hydrogen damage mechanisms may operate i.e., HTHA (Ref. [1]). See API 571 and API RP941 for further information on HTHA in steels. Note that for all metallic materials, at high temperatures, creep damage may be of concern.

f. The table is valid from the minimum design temperature as given in ASME B31.12 mandatory appendix IX, table IX-1. See also table GR-2.1.2-1 in ASME B31.12 for Charpy impact testing requirements depending on the design temperature (Ref. [1]). As a guide, for carbon and micro alloyed steels the minimum design temperature ranges between -48°C and -29°C, with additional impact testing, if required by ASME B31.12.

g. Permitted steels are allowed only if stresses do not exceed limits as defined in ASME B31.12. Refer to ASME B31.12 Mandatory appendix IX: Allowable stress and quality factors for allowable metallic piping and bolting materials. The appendix is to be used with relevant design stress chapters.

h. Refer to ASME B31.12 Table GR-2.1.1-1 for allowable metals/alloys specifications for IP (Industrial piping). Allowable grades in appendix IX Table IX-1A are many e.g., A135 grade A (pipes and tubes), A516 grade 55 (plates and sheets), A234 grade WPB (forgings and fittings), A216 grade WCB (castings). Note see appendix IX table IX-4 for allowable grades of bolting materials. Suitable component standards for industrial piping are given in Table IP-8.1.1-1 of ASME B31.12.

i. Refer to ASME B31.12 section GR-3 and IP chapters for welding/brazing requirements i.e., welding guidance, preheat, post weld heat treatment, hardness testing and hardness limits.

j. Refer to ASME B31.12 sections GR-3.9, GR3.9.1, and IP-9.12 for requirements on cold forming or cold bending.
k. For carbon and alloy steels ASME B31.12 requires specific heat treatment after cold bending and cold forming if certain conditions of strain are met as described in section GR. 3.9.1.
l. All steels may suffer from corrosion (aqueous) e.g., due to the atmosphere, contact with rainwater, seawater etc. Use of steels in gaseous H2 should therefore consider threats from external corrosion or accidental internal corrosion.

8.2 USE OF STAINLESS STEELS IN H2 GAS

Definitions

Stainless steels are mainly alloys of iron and chromium (typically 16-22 wt%) with nickel present in some alloy groups (7-13 wt%). The various types of stainless steel are briefly highlighted below:

- ✓ **Austenitic stainless steels** have a face centred cubic crystal structure (FCC). The FCC structure means that these steels possess good toughness even at very low temperatures (stable grades only). These include the 300 series stainless steels having around 16-19 wt% Cr and more than 7% Ni. These include type 304, 304L, 316, 316L, 304N, and type 347. Note that "L" signifies low carbon versions, suitable for welding. Versions with the symbol "N" indicate with extra nitrogen addition for strength or corrosion resistance. Versions with reduced nickel (low cost), are included in the 200 series, where Ni is replaced by Mn and N alloying. Examples include type 201LN, 201. Finally, highly alloyed austenitic stainless steels also exist in which the strength is raised even more by fine particles (precipitates). An example is grade A-286.
- ✓ **Ferritic stainless steels** have a BCC crystal structure and therefore display low toughness at low temperature like steels. Ferritic stainless steels include the 400 series stainless steels with typically 11-19 wt% Cr and little or no Ni additions. Examples include types 410L, 434, and 441.
- ✓ **Martensitic stainless steels** are 400 series stainless steels which are heat treatable by quenching and tempering, allowing the formation of a hard and strong "tempered martensitic" structure. Examples include type 410, 420, and F6NM. They display low toughness at low temperatures.
- ✓ **Martensitic precipitation hardened stainless steels** are martensitic stainless steels with high strength due to precipitates. Examples include 17-4PH, 17-7PH, and 15-5PH. They display low toughness at low temperatures.
- ✓ **Duplex stainless steels** possess a mixed structure of around 50% ferrite (BCC crystal structure) and 50% austenite (FCC crystal structure). They also exhibit low toughness at low temperatures. These alloys combine the beneficial effect of ferritic grades (strength) and austenitic stainless steels (corrosion resistance). Different types of duplex stainless steel exist. Standard grades include types 2205. Lean (cheaper) duplex grades include types 2101 and 2304. Super duplex grades with high corrosion resistance include types 2507 and 4501.

Overview of stainless steels compatibility with H2 gas

The performance of stainless-steel grades in H2 gas depends on the type of stainless steel. In addition, for austenitic stainless steels the compatibility depends on the steel chemistry.

Generally, the 300 series austenitic stainless steels are suitable for H2 gas service. However, this suitability depends on the stability of the specific chemistry under consideration. Thus, unstable austenitic stainless steels may transform to a brittle structure (martensite), at sufficiently low temperatures or even at room temperature, if a sufficient plastic strain is applied. This plastic strain or "cold work" can be applied via forming of a component or by bending at room temperature, or even by over tightening of bolts or by machining operations.

To avoid this brittle structure in service, which is highly susceptible to hydrogen embrittlement, the steel chemistry can be controlled to improve the thermal and mechanical stability. Thus, one may calculate a so-called austenite stability factor to understand if a specific actual chemistry is at-risk. For 300 series stainless steels the mechanical stability factor is given by the Post and Eberly relationship (Ref. [20]):

$$\Delta = Ni + 0.5Mn + 35C - 0.0833(Cr + 1.5Mo - 20)^2 - 12$$

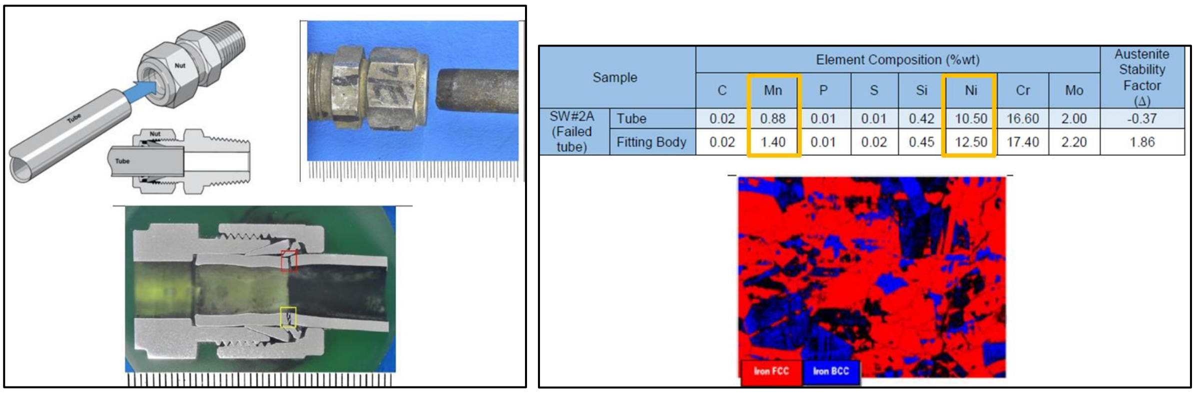
Where element amounts are in wt%. A positive delta factor (Δ) indicates the alloy composition is stable and suitable for H2 service. A negative value indicates that the alloy is likely to transform to the brittle structure when severely strained (80% cold work). According to the literature, 300 series stainless steels are compatible with H2 gas if the Ni content is at least 10.5 wt% (Ref. [20]). Other references i.e., ASME B31.12, declares that type 316 stainless steel is a good choice when the Ni content is more than 12 wt% (Ref. [1]). Such statements are helpful, but more detailed insights can be obtained by analyzing specific chemistries. Table 2.2 below shows the calculated stability factor for the most common weldable 300 stainless steels.

Table 8.2: Austenite stability factor for common weldable 300 series stainless steels. Note element amounts are in wt%.

Grade	C	Mn	Cr	Mo	Ni	Δ
EN 1.4306 (Type 304L)	0.02	1.0	18.0	-	10.5 (typical)	-0.6
	0.02	1.0	18.0	-	11.5 (high)	+0.4
EN 1.4404 (Type 316L)	0.02	1.0	17.0	2.0	10.5 (typical)	-0.3
	0.02	1.0	17.0	2.0	11.5 (high)	+0.7

As has can be seen, for type 304L a high Ni content would be required to obtain a positive delta factor. For type 316L a typical value is borderline, whilst a high Ni level easily guarantees a positive delta factor (thanks to Mo addition). From this analysis it can clearly be seen that actual materials datasheets are essential when assessing a specific grade for H2 gas service. Moreover, the key elements (which have most effect) are Ni, Mn, Mo, and Cr.

The role of the delta factor can be appreciated further by considering an actual real-world example as shown by Figure 8.2 below. Thus, in a refinery hydroprocessing unit type 316L was used for instrumentation tubing (compression fitting tube and body). After exposure to hydrogen gas at 173 bar at 55°C, the fitting failed. The failure caused a small H2 leak and fire. The refinery unit was shut down for 10 days as a result (Ref. [25]).



Sample		Element Composition (%wt)								Austenite Stability Factor (Δ)
		C	Mn	P	S	Si	Ni	Cr	Mo	
SW#2A (Failed tube)	Tube	0.02	0.88	0.01	0.01	0.42	10.50	16.60	2.00	-0.37
	Fitting Body	0.02	1.40	0.01	0.02	0.45	12.50	17.40	2.20	1.86

A) **B)**

Figure 8.2: Failure of type 316L tubing in 173 bar H2 at 55°C. A) Broken fitting. B) Post-test analysis of tube and fitting body (Ref. [25]).

Post-test analysis showed that the failure was caused by overtightening of the fitting by the operator. This caused formation of the brittle structure in the tube metal (as seen by the blue colour in the micrograph image). The brittle structure failed due to hydrogen embrittlement. Chemical analysis revealed that the tube had a negative delta factor i.e., lower austenite stability. It is important to note that both the fitting body and tube conformed to the 316L grade chemical limits. Thus, only by analysing the materials data sheet could the austenite stability be valuated correctly.

Figure 8.3 below shows an example of real data generated from round bar tensile tests in hydrogen gas comparing different stainless steels. Note that the resistance to hydrogen embrittlement is expressed as a ductility ratio. This intends the reduction of cross section (at failure) in hydrogen divided by that in air. Thus, a value of 1.0 signifies no loss of ductility.

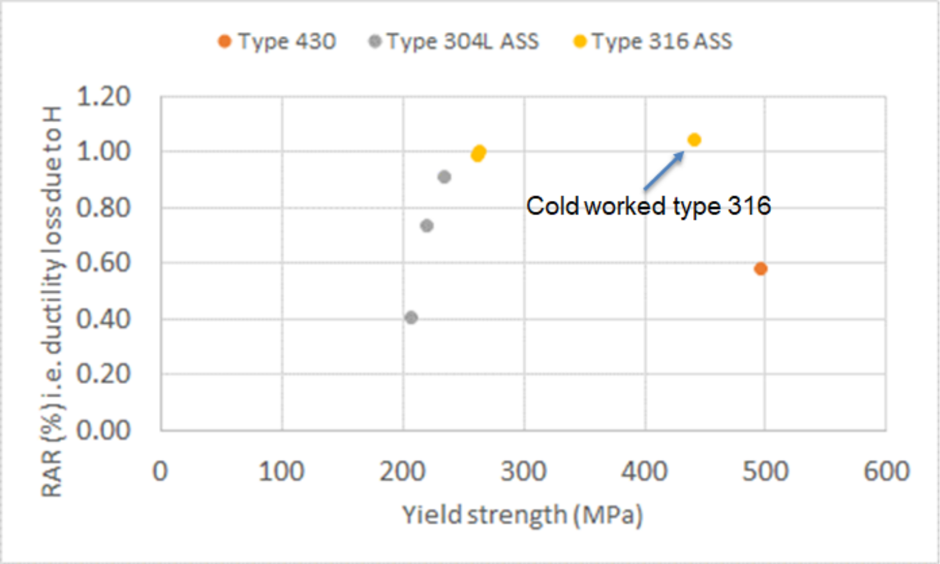


Figure 8.3: Resistance of stainless steels to hydrogen embrittlement in H2 gas at pressures of 690 bar at room temperature. Data was elaborated from reference [19].

As can be seen from Figure 8.3, type 304L reveals a variable resistance to hydrogen embrittlement. This behaviour is due to compositional differences (each data point is a different composition), giving a variable delta factor. On the other hand, the type 316 reveals very good resistance, due to a richer chemistry and positive delta factor. It is also shown that cold work before the tensile test (to increase strength) has not reduced the resistance of the type 316, in line with high austenite mechanical stability and positive delta factor. Finally, it can be seen that the high strength type 430 (ferritic stainless) has a relatively low resistance to hydrogen embrittlement, compared to most of the 300 series chemistries tested.

An additional issue for austenitic stainless steels is the presence of delta ferrite in the metal structure. This delta ferrite can be present in cast components or formed during welding. Since this ferrite has a BCC crystal structure hydrogen may easily move within this phase and embrittle. Thus, it has been observed that higher delta ferrite levels give rise to a lower hydrogen embrittlement resistance in 300 series austenitic stainless steels (Ref. [21]). This concern is reflected in some standards i.e., SAE J2579 (Ref. [24]), where it is recommended that components (weld and base material) possess a fraction of magnetic phase (BCC component), of maximum 3%. Finally, to reduce the amount of delta ferrite requires proper controls of heat treatment and welding procedures, including the correct choice of filler metal.

Other stainless steels including ferritic, martensitic, precipitation hardened martensitic grades, and duplex, have a low resistance to hydrogen embrittlement (Refs. [1], [20], [22], and [23]). In addition, there is a lack of comprehensive test data for such materials (Ref. [1]). Thus, their use for H2 gas service is not recommended. Likewise, the austenitic stainless steels with precipitation hardening (e.g., grade A-286), has a low resistance to hydrogen embrittlement, and therefore is not compatible with H2 service (Ref. [1]).

Material selection table for stainless steels in H2 gas

Table 2.3 below shows the materials selection table for stainless steels. The table shows the resistance of each group of metals/alloys to hydrogen embrittlement. The table shall be read taking into consideration the detailed notes under the table.

Table 8.3 Materials selection table for stainless steels in dry H2 gas service.

Metal/alloy	H2 compatible	H2 compatible but not recommended	Not H2 compatible	Remarks
Selected 300 series Austenitic stainless steels	Refs. [1], [20], [22], and [23]			Avoid highly metastable grades like type 301 and 302. Use grades listed in ASME B31.12. Use chemistries with positive delta factor when significant plastic strain can be present e.g., due to cold work/forming/bending, or accidental damage. Limit delta ferrite content i.e., max 3%.
Precipitation hardened austenitic stainless steel			Ref. [1]	Poor resistance to HE of A-286 grade. This class of alloys not suitable for Hydrogen service.
Ferritic stainless steels			Refs. [1], [20], [22], and [23]	Poor performance of ferritic, martensitic, precipitation hardened grades and duplex in hydrogen gas. Also lack of comprehensive testing data.
Martensitic stainless steels and precipitation hardened versions			Refs. [1], [20], [22], and [23]	
Duplex stainless steels			Refs. [1], [20], [22], and [23]	

Notes

a. The table is valid only for dry H2 gas service. Tables shall not be used for conditions where water condensation occurs (Ref. [1]).

b. The table is not valid for when H2 is mixed with gases that may promote hydrogen embrittlement e.g., with H2S or CO2 or H2O.

c. The maximum H2 pressure allowed is 1034 bar for all compatible steels unless otherwise noted (Ref. [1]). Maximum 414 bar for stainless steels supplied to ASTM A182, ASTM A312, or equivalents.

d. Note that the maximum H2 pressures given may be exceeded if the material is qualified by suitable testing in H2 gas (Ref. [1]).

e. At higher temperatures (significantly above room temperature) hydrogen embrittlement will be less of a concern for stainless steels. For allowable austenitic stainless steels, see ASME B31.12 mandatory appendix IX for allowable stress for different grades as a function of design temperature. Note that for all metallic materials, at high temperatures creep damage may be of concern.

f. The table is valid from the minimum design temperature as given in ASME B31.12 mandatory appendix IX, table IX-1. See also table GR-2.1.2-1 in ASME B31.12 for Charpy impact testing requirements depending on the design temperature (Ref. [1]). As a guide, for austenitic stainless steels the minimum design temperature ranges between -198°C and -253°C, with additional impact testing, if required by ASME B31.12.

g. Permitted stainless steels are allowed only if stresses do not exceed limits as defined in ASME B31.12. Refer to ASME B31.12 Mandatory appendix IX: Allowable stress and quality factors for allowable metallic piping and bolting materials. The appendix is to be used with relevant design stress chapters.

h. Refer to ASME B31.12 Table GR-2.1.1-1 for allowable metals/alloys specifications for IP (Industrial piping). Allowable grades in B31.12 appendix IX table IX-1A include types 304, 304N, 304L, 316, 316L, 347 (pipes and tubes), 304, 304L, 316, 316L, 347 (plates and sheets + forgings and fittings), A351- selected grades for castings. Note see appendix IX table IX-4 for allowable grades of bolting materials.

i. Care must be taken when selecting these materials as some austenitic stainless steels may transform to martensite (a brittle constituent) at low temperatures or due to significant plastic strain (above the yield stress) even at around room temperature. This brittle constituent is highly susceptible to hydrogen embrittlement. Plastic strains can be due to cold bending or forming or even to due to poor machining or overtightening of bolts. To avoid this issue the austenite stability factor (delta) can be calculated from a suppliers' materials data sheet ($\Delta = \boldsymbol{Ni + 0.5Mn + 35C - 0.0833(Cr + 1.5Mo - 20)^2 - 12}$, element amounts in wt%), accepting only positive values when plastic strains are present. It should be noted that ASTM B31.12

recommends type 316 or type 316L, where the Ni content is above 12.0 wt%. Such an alloy is expected to have a positive delta value.

j. Refer to ASME B31.12 section GR-3 and IP chapters for welding/brazing requirements i.e., welding guidance, preheat, post weld heat treatment.

k. Refer to ASME B31.12 sections GR-3.9, GR3.9.1, and IP-9.12 for requirements on cold forming or cold bending. For suitable listed austenitic stainless steels, ASME B31.12 allows cold bending and forming- see section GR-3.9 and GR-3.9.1. Cautionary note- Cold bending or cold forming without annealing may lead to a risk of brittle martensite formation if the strain is high enough for alloys with a negative delta factor- see point 9) above.

l. Although austenitic stainless steels are much more resistant to aqueous corrosion than steels, care should be taken in their selection for resistance to such corrosion (external or accidental internal). For example, type 304L has a much lower resistance to corrosion in salt water compared to type 316L.

m. Austenitic stainless steels may suffer from chloride stress corrosion cracking (not due to hydrogen). This form of cracking (externally or internally) is due to a combination of stress and aqueous corrosion in the presence of chloride. Sources of chloride include sea water, wet air in coastal areas. Other chloride sources include wrong selection of materials for thermal insulation, marking inks, paints, labels, tapes, glues (ASME B31.12 GR-2.1.4). In general, this cracking occurs above metal temperatures of 60°C.

n. The delta ferrite (constituent with BCC structure) may be present in some austenitic stainless steels as a result of manufacturing e.g., in cast alloys or welding. This delta ferrite can reduce resistance to hydrogen embrittlement. The delta ferrite is minimized by correct heat treatment and proper welding procedures including choice of filler. As a recommendation supplied materials and components should have a delta ferrite + martensite content (magnetic phases) of less than 3% by volume (weld and base material). This value is recommended in SAE J2579 (Ref. [24]).

o. There is some evidence that high nitrogen levels may promote HE in austenitic stainless steels. Thus, the N level is recommended to be limited to 0.25 wt% (Ref. [24]).

p. 200 series austenitic stainless steels may or may not be suitable for dry hydrogen gas service. At the present time there is not sufficient information available to make a judgement. Thus, these alloys shall not be used unless subjected to a suitable qualification testing program, considering also other threats e.g., corrosion and stress-corrosion resistance.

8.3 USE OF COPPER AND COPPER ALLOYS IN H2 GAS

Definitions

Copper and its alloys generally possess an FCC crystal structure. Generally, the copper content is at least 55% (Ref. [20]). The various types are briefly described below:

- ✓ **Copper** refers to high purity copper with no residual oxygen. Examples include grades C10200 (oxygen-free copper), C12000 and C12200 (phosphorus deoxidized coppers).
- ✓ **Brasses** are a large family of copper-zinc based alloys. Some examples include red brass pipe (C23000 grade) and forging brass (C37700).
- ✓ **Bronzes** include a large family of copper-tin based alloys including other Cu alloys with Si, Mn, and Al. Some examples include Al-bronze plates and sheet (grade C61400) and Mn-bronze forgings (grade C67500).
- ✓ **Copper-Nickel alloys** include 90Cu-10Ni pipes (grade C70600), and 70Cu-30Ni plates and sheets (grade C71500).
- ✓ **Copper-Beryllium alloys** are a small family of copper alloys. Common grades include C17200 sheets.

Overview of Copper and Copper alloys compatibility with H2 gas

Compared to steels and stainless steels, much less information is available concerning the compatibility of copper and its alloys with H2 gas. The mechanism by which copper can be embrittled from hydrogen gas involves the presence of dissolved oxygen or oxides within copper that can react with hydrogen gas. This leads to the formation of water within the metal structure, resulting in pores that promotes failure [1]. At temperatures higher than 370°C the steam pressure is enough to cause cracking [9]. Despite this concern, most copper and copper alloys are deoxidized, and therefore are suitable for H2 gas service.

Oxygen free copper is considered to be highly resistant to H2 gas embrittlement (Ref. [22]). Brass (Cu-Zn) and Bronze (Cu-Sn) are considered resistant to H2 gas (Ref. [23]). Cu-Be alloys are resistant to H2 gas, but production is limited due to Be toxicity (Ref. [21]). Finally, caution should be exercised when selecting Cu-Ni alloys due to known hydrogen embrittlement issues with Ni alloys (Ref. [22]).

Figure 8.4 below shows an example of the few existing real tensile test data in hydrogen gas for copper. Note that the resistance to hydrogen embrittlement is expressed as a ductility ratio. This intends the reduction of cross section (at failure) in hydrogen divided by that in air. Thus, a value of 1.0 signifies no loss of ductility.

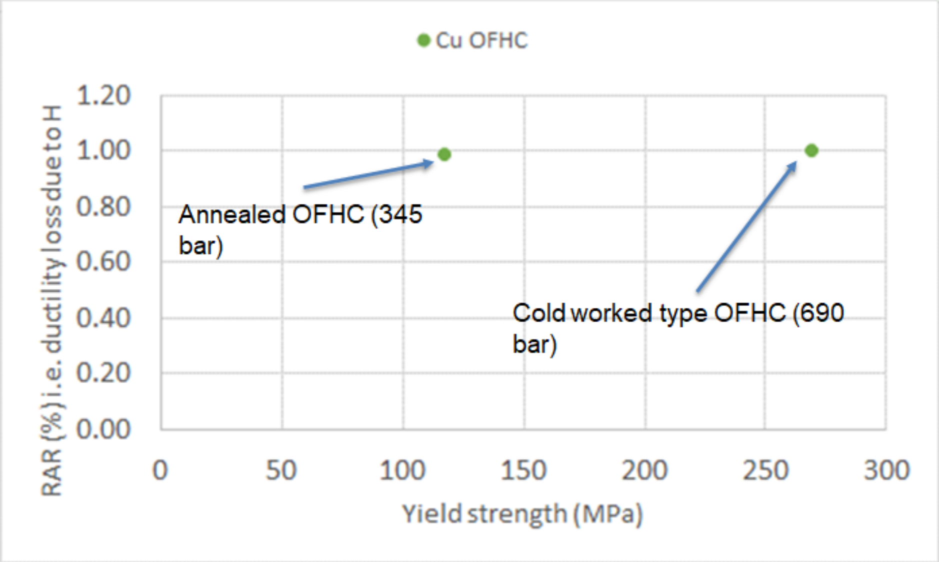


Figure 8.4: Resistance of oxygen free high conductivity (OFHC) copper to hydrogen embrittlement in H2 gas at room temperature. Data was elaborated from reference [19].

As can be seen from Figure 8.4, both annealed OFHC copper and the cold worked version give excellent resistance to hydrogen gas embrittlement.

Material selection table for copper and its alloys in H2 gas

Table 2.4 below shows the materials selection table for copper and copper alloys. The table shows the resistance of each group of metals/alloys to hydrogen embrittlement. The table shall be read taking into consideration the detailed notes under the table.

Table 8.4: Materials selection table for copper and its alloys in dry H_2 gas service.

Metal/alloy	H2 compatible	H2 compatible but not recommended	Not H2 compatible	Remarks
Copper	Refs. ([1], [20], and [23])			Use oxygen free or deoxidized copper alloys. Use grades listed in ASME B31.12.
Brasses	Refs. ([1] and [23])			
Bronzes	Refs. ([1] and [23])			
Copper-Nickel alloys		Ref. [22]		Although Cu-Ni alloys are listed in ASME B31.12, they should be used with caution due to presence of Ni which may degrade H embrittlement resistance (Ref. [22].
Copper-Beryllium		Refs. [21] and [23]		Not listed in ASME B31.12. Toxicity issues with Be fume or powder from manufacturing, machining, welding (Ref. [21]).

Notes

a. The table is valid only for dry H2 gas service. Tables shall not be used for conditions where water condensation occurs (Ref. [1]).
b. The table is not valid for when H2 is mixed with gases that may promote hydrogen embrittlement e.g., with H2S or CO2 or H2O.
c. The maximum H2 pressure allowed is 1034 bar for all compatible Cu and Cu alloys (Ref. [1]).
d. Note that the maximum H2 pressures given may be exceeded if the material is qualified by suitable testing in H2 gas (Ref. [1]).
e. At higher temperatures (significantly above room temperature) hydrogen embrittlement will be less of a concern for Cu and Cu alloys. For allowable Cu and Cu alloys, see ASME B31.12 mandatory appendix IX for allowable stress for different grades as a function of design temperature. Note that for all metallic materials, at high temperatures creep damage may be of concern.
f. The table is valid from the minimum design temperature as given in ASME B31.12 mandatory appendix IX, table IX-1. See also table GR-2.1.2-1 in ASME B31.12 for Charpy impact testing requirements depending on the design temperature (Ref. [1]). As a guide, for Cu and its alloys the minimum design temperature ranges between -198°C and -269°C, with additional impact testing, if required by ASME B31.12.
g. Permitted Cu and Cu alloys are allowed only if stresses do not exceed limits as defined in ASME B31.12. Refer to ASME B31.12 Mandatory appendix IX: Allowable stress and quality factors for allowable metallic piping and bolting materials. The appendix is to be used with relevant design stress chapters.
h. Refer to ASME B31.12 Table GR-2.1.1-1 for allowable metals/alloys specifications for IP (Industrial piping). Allowable grades in B31.12 appendix IX table IX-1A include Cu pipe and tube and red brass pipe, Cu and bronze for plates and sheets, Cu, bronze, and brass for forgings, and bronze castings. Note see appendix IX table IX-4 for allowable grades of bolting materials.
i. Refer to ASME B31.12 section GR-3 and IP chapters for welding/brazing requirements i.e., welding guidance, preheat, post weld heat treatment.
j. Refer to ASME B31.12 sections GR-3.9, GR3.9.1, and IP-9.12 for requirements on cold forming or cold bending. For suitable listed materials, ASME B31.12 allows cold bending and forming- see section GR-3.9 and GR-3.9.1.
k. Oxygen dissolved in copper or as oxides can react with H2. These forms water leading to pores and fissures that promote failure. Thus, oxygen free grades of copper must be used for H2 gas service. Most Cu alloys are deoxidized so do not suffer from HE (Refs. [1] and [20]).
l. Material selection of copper alloys should also consider other types of damage i.e., aqueous corrosion, de zincification (for brasses) where Zn may dissolve in sea water or polluted water, risk of stress corrosion cracking in ammonia/ammonium compounds (known as season cracking), acetylide formation when exposed to acetylene (Ref. [1]).

8.4 USE OF ALUMINIUM AND ALUMINIUM ALLOYS IN H2 GAS

Definitions

Aluminium and its alloys possess an FCC crystal structure. The various types are briefly described below:

- ✓ **1xxx series wrought and 1xx.x series cast:** This refers to pure Al (at least 99%). Example wrought grade is grade 1100. Example cast grade is 100.0.
- ✓ **2xxx series wrought and 2xx.x series cast:** These are heat treatable Al alloys with Cu as major alloying element. Example wrought grade is grade 2024. Example cast grade is 201.0.
- ✓ **3xxx series wrought and 3xx.x series cast:** These are non-heat treatable Al alloys with Mn as major alloying element for wrought series. For cast series major alloying elements are Si + (Cu and/or Mg). Example wrought grade is 3003 and example cast grade is 356.0.
- ✓ **4xxx series wrought and 4xx.x series cast:** These are non-heat treatable Al alloys with Si as major element. Example wrought grade is 4043, and example cast grade is 443.0.
- ✓ **5xxx series wrought and 5xx.x series cast:** These are non-heat treatable Al alloys with Mg as major element. Example wrought grade is 5052, and example cast grade is 514.0.
- ✓ **6xxx series wrought (cast versions do not exist):** These are heat treatable Al alloys with Mg and Si as major alloying elements. Example wrought grade is 6061.
- ✓ **7xxx series wrought and 7xx.x series cast:** These are heat treatable Al alloys with Zn as the major alloying element. Example wrought grade is 7075 and example cast grade is 713.0.
- ✓ **8xxx series wrought and 8xx.x + 9xx.x series cast:** For wrought series 8xxx these are Al alloys with other elements e.g., Li and Cu together. For the cast series 8xx.x are Al alloys with Sn as the major alloying element. For the cast series 9xx.x, these are Al alloys with other elements.

Overview of aluminium and aluminium alloys compatibility with H2 gas

As for copper, limited information is available concerning the compatibility of aluminium and its alloys with H2 gas. Generally, aluminium alloys are considered to be compatible with dry H2 gas (Refs. [1], [22], and [23]). However, if there is liquid water or water vapour present then hydrogen entry is facilitated. For high strength aluminium alloys exposed to wet H2, hydrogen embrittlement is then a concern (Refs. [1] and [21]).

Figure 8.5 below shows an example of real tensile test data in hydrogen gas for aluminium and its alloys. Note that the resistance to hydrogen embrittlement is expressed as a ductility ratio. This intends the reduction of cross section (at failure) in hydrogen divided by that in air. Thus, a value of 1.0 signifies no loss of ductility.

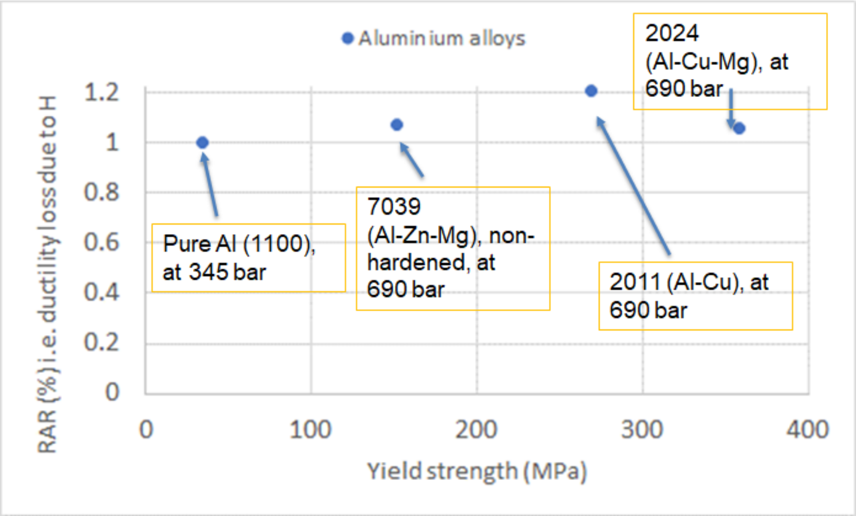


Figure 8.5: Resistance of aluminium and its alloys to hydrogen embrittlement in H2 gas at room temperature. Data was elaborated from reference [19].

As can be seen from Figure 8.5, both pure aluminium and the shown alloys have excellent resistance to hydrogen gas embrittlement. Note that the above alloys do not appear in the material selection table shown below, since the stress corrosion resistance would need to be evaluated.

Material selection table for aluminium and its alloys in H2 gas

Table 2.5 below shows the materials selection table for aluminium and its alloys. The table shows the resistance of each group of metals/alloys to hydrogen embrittlement. The table must be read taking into consideration the detailed notes under the table.

Table 8.5: Materials selection table for aluminium and its alloys in dry H2 gas service.

Metal/alloy	H2 compatible	H2 compatible but not recommended	Not H2 compatible	Remarks
Commercially pure wrought Al (1xxx series)	Refs. [1] and [23])			See allowable grades in ASME B31.12
Wrought Al-Mn alloys (3xxx series)	🟩			See allowable grades in ASME B31.12
Wrought Al-Mg alloys (5xxx series)	🟩			Some grades cannot be used above 66°C. See allowable grades in ASME B31.12
Wrought Al-Mg-Si alloys (6xxx series)	🟩			See allowable grades in ASME B31.12
Cast Al alloys	Ref. [1]			ASME B31.12 provides design stresses only for two grades i.e., 443.0 and 356.0.

Notes

a. The table is valid only for dry H2 gas service. Tables shall not be used for conditions where water condensation occurs (Ref. [1]). For acceptable aluminium alloys water vapour must be absent.

b. The table is not valid for when H2 is mixed with gases that may promote hydrogen embrittlement e.g., with H2S or CO2 or H2O.

c. The maximum H2 pressure allowed is 1034 bar for all compatible alloys (Ref. [1]).

d. Note that the maximum H2 pressures given may be exceeded if the material is qualified by suitable testing in H2 gas (Ref. [1]).

e. At higher temperatures (significantly above room temperature) hydrogen embrittlement will be less of a concern. For allowable alloys, see ASME B31.12 mandatory appendix IX for allowable stress for different grades as a function of design temperature. Note that for all metallic materials, at high temperatures creep damage may be of concern.

f. The table is valid from the minimum design temperature as given in ASME B31.12 mandatory appendix IX, table IX-1. See also table GR-2.1.2-1 in ASME B31.12 for Charpy impact testing requirements depending on the design temperature (Ref. [1]). As a guide, for Al and its alloys the minimum design temperature is usually -269°C, with additional impact testing, if required by ASME B31.12.

g. Permitted alloys are allowed only if stresses do not exceed limits as defined in ASME B31.12. Refer to ASME B31.12 Mandatory appendix IX: Allowable stress and quality factors for allowable metallic piping and bolting materials. The appendix is to be used with relevant design stress chapters.

h. Refer to ASME B31.12 Table GR-2.1.1-1 for allowable metals/alloys specifications for IP (Industrial piping). Allowable wrought grades + heat treatments in B31.12 appendix IX table IX-1A include e.g., 1100, 3003, 5052, 6061 for seamless pipes and tubes, grades 1100, 3003, 5050, 6061 for plates and sheet, grades 3003, 6061, WP1100 for forgings and fittings. Allowable grades + heat treatments for castings in table IX-A are only 443.0 and 356.0. Note see appendix IX table IX-4 for allowable grades of bolting materials.

i. Refer to ASME B31.12 section GR-3 and IP chapters for welding/brazing requirements i.e., welding guidance, preheat, post weld heat treatment.

j. Refer to ASME B31.12 sections GR-3.9, GR3.9.1, and IP-9.12 for requirements on cold forming or cold bending. For suitable listed materials, ASME B31.12 allows cold bending and forming- see section GR-3.9 and GR-3.9.1.

k. Note that SAE J2579 Surface Vehicle Standard: Standard for fuel systems in fuel cell and other hydrogen vehicles", considers grade 6061 in several tempers as acceptable for dry H2 gas service (Ref. [24]).

l. Aluminium wrought alloy grades 5083, 5086, 5154 and 5456 are susceptible to exfoliation (intergranular attack leading to build up of corrosion products which causes separation of grains (leafing effect), above 66°C. Therefore, they shall not be used above this temperature (Ref. [1]).

m. Al alloy materials selection should also consider compatibility of Al threaded joints with thread compounds (Ref. [1]).

n. Al alloys may suffer corrosion from building materials (alkaline) i.e., lime, plaster, mortar, concrete (Ref. [1]).

o. Some high strength Al alloys may suffer from stress corrosion cracking (action of stress+ corrosion leading to cracking) in wet air or aqueous environments (e.g., 6082, Ref. [24]). This should be considered when selecting these alloys.

p. Other wrought and cast Al alloys, not listed in ASME B31.12 mandatory appendix IX, may be suitable for dry hydrogen gas service. However, at the present time there is not sufficient information available to make a judgement. Use of such alloys should only be considered following a suitable qualification testing program, considering also other threats e.g., corrosion and stress-corrosion resistance (e.g., testing based on HPIS E-103:2018).

8.5 USE OF NICKEL, TITANIUM AND THEIR ALLOYS IN H2 GAS

Definitions

Nickel and its alloys possess an FCC crystal structure. The nickel content is usually at least 30 wt% (Ref. [20]). The various types are briefly described below:

- ✓ **Pure Ni** (e.g., grade N02200).
- ✓ **Ni-Cu alloys** (e.g., Monel grade 400).
- ✓ **Ni-Fe alloys** (e.g., Invar).
- ✓ **Ni-Mo alloys** (e.g., grade B-2).
- ✓ **Ni-Cr based alloys**, including alloy 600, alloy X-750, alloy 718, alloy 945X.
- ✓ **Ni-Cr-Fe alloys**, including alloy 800, and Ni-Cr-Fe-Mo-Cu alloys (e.g., alloy 825).
- ✓ **Ni-Cr-Mo alloys**, including alloy C-276.
- ✓ **Ni-Cr-Co alloys**, including alloy 617.
- ✓ **Ni-Ti alloys**, including Nitinol.

Titanium and its alloys can be divided into different groups as outlined below:

- ✓ **Commercially pure Ti grades**: These have an HCP crystal structure (alpha). Examples include ASTM grade 1.
- ✓ **Commercially pure grades modified with additions of Pd and Ru**: These include Ti-0.15Pd (ASTM grade 7) and Ti-0.1Ru (ASTM grade 26).
- ✓ **Alpha and near Alpha alloys**: These have mainly the HCP crystal structure (alpha). These include Ti-3Al-2.5V (ASTM grade 9) and Ti-5Al-2.5Sn (ASTM grade 6).
- ✓ **Alpha-Beta alloys**: These have a mixture of the HCP structure (alpha) and the BCC structures (beta). These include Ti-6Al-4V (ASTM grade 5).
- ✓ **Beta and near Beta alloys**: These have mainly the BCC crystal structure (beta). These include Ti-10V-2Fe-3Al.

Overview of nickel, titanium and their alloys compatibility with H2 gas

Nickel alloys are not considered compatible with hydrogen gas (Refs. [1], [21], and [23]). Nickel and its alloys all can suffer from hydrogen embrittlement.

Concerning titanium and its alloys the literature provides a complex picture. The key standards and guidelines provide contradictory information. Thus, the earlier ASME technical reference (Ref. [22]) and review publications (Ref. [21]), declare that Ti and its alloys are severely embrittled in H2 gas service. Moreover, academic publications highlight the susceptibility of Ti alloys to hydrogen embrittlement and embrittlement via hydriding (Ref. [26]). On the other hand, ASME B31.12 (Ref. [1]) and the NASA technical reference (Ref. [23]), suggests that Ti and its alloys can be used in H2 gas. ASME B31.12 does not provide any details on use of Ti alloys in terms of temperature limits or maximum stress levels. In section GR-2.14 of that document it is also stated that the ""possibility of deterioration of titanium and its alloys exists". Thus, a confusing picture of Ti and its alloys performance exists.

Other insights can be found by exploring the experience in other industries. Thus ISO15156-3 (a materials selection standard for the oil and gas industry considering aqueous H2S acidic environments, where hydrogen damage is promoted), states that Ti and its alloys can suffer hydrogen damage above 80°C (Ref. [27]). Refinery industry standard API 571 refers to hydriding damage above 70°C for Ti and its alloys when exposed to aqueous acidic H2S containing environments (Ref. [28]). Moreover, the same document indicates that such hydriding can occur about 177°C for Ti and its alloys exposed to hydrogen gas (Ref. [28]). Finally, a technical guide from a leading Ti manufacturer, states that hydrogen damage from H2 gas requires a combination of high temperature and pressure, admitting also, that Ti and its alloys are not suitable when exposed to dry H2 gas (Ref. [29]).

Overall, based on the conflicting guidance and lack of a detailed operating window (temperature, pressure, stress level, etc.), it is concluded that Ti and its alloys are not considered for H2 gas service without a case-by-case evaluation, also employing tests to qualify each alloy for the intended service environment.

Material selection table for nickel, titanium, and their alloys in H2 gas

Table 2.6 below shows the materials selection table for aluminium and its alloys. The table shows the resistance of each group of metals/alloys to hydrogen embrittlement. The table shall be read taking into consideration the detailed notes under the table.

Table 8.6: Materials selection table for nickel, titanium, and their alloys in dry H2 gas service.

Metal/alloy	H2 compatible	H2 compatible but not recommended	Not H2 compatible	Remarks
Pure Ni and Ni alloys			Refs ([1], [20], and [23])	Ni and Ni alloys are all highly susceptible and shall not be used for H2 gas service. ASME B31.12 lists Monel (alloy N04400). However, this is for use in liquid hydrogen service only.
Pure Ti and Ti alloys			Refs ([21], [22], [27], [28], and [29])	Ti alloys can be susceptible to hydrogen embrittlement and hydride formation in H2 gas. Lack of clear guidance in literature on safe use in H2.

RINA Consulting S.p.A. | Società soggetta a direzione e coordinamento amministrativo e finanziario del socio unico RINA S.p.A.
Via Cecchi, 6 - 16129 GENOVA | P. +39 010 31961 | rinaconsulting@rina.org | www.rina.org
C.F./P. IVA/R.I. Genova N. 03476550102 | Cap. Soc. € 20.000.000,00 i.v.