RISK ASSESSMENT AND MANAGEMENT
OF STRATEGIC ENERGY TECHNOLOGIES

ENERO 3rd SCIENTIFIC WORKSHOP

BRUSSELS, 5 March 2010
UNIVERSITY FOUNDATION, rue d' Egmontstraat 11,

# Materials and Hydrogen

Dr. Ing. I. Azkarate
iazkara@inasmet.es

---

## Index

# 1.- General aspects

## Material selection criteria

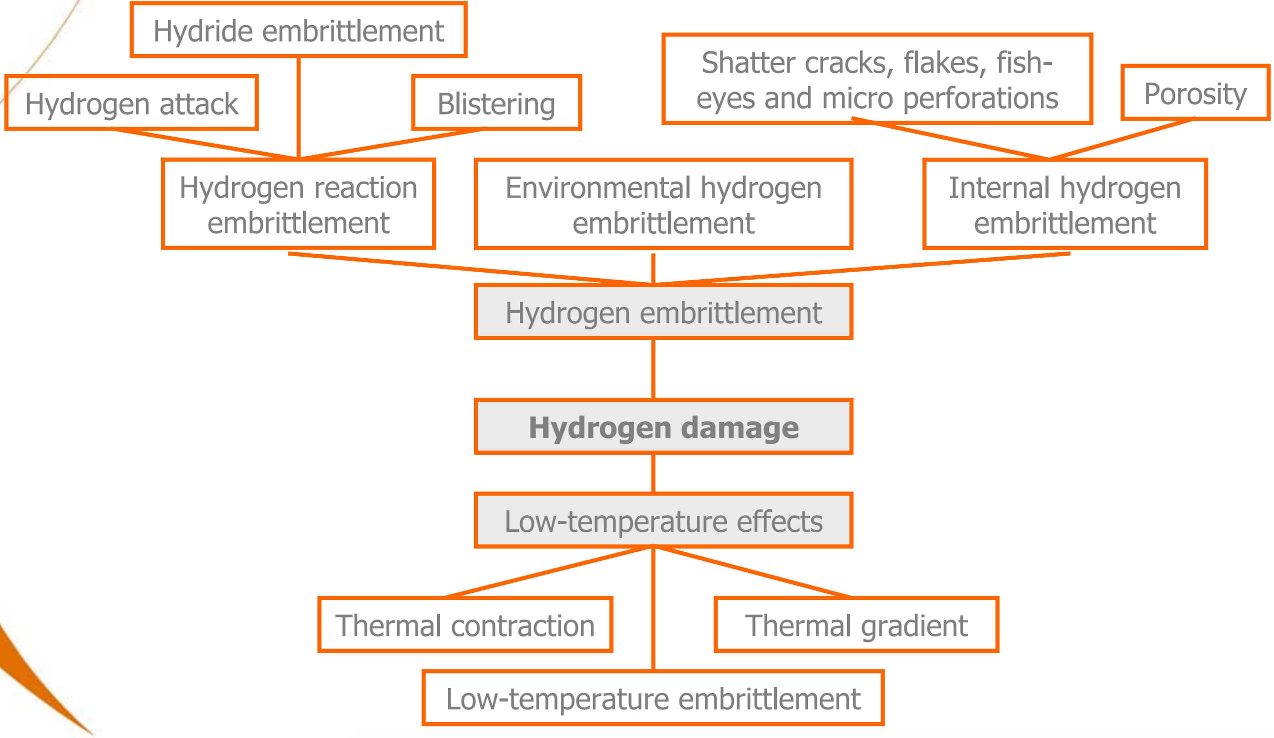
- Compatibility with hydrogen;
- Compatibility with adjoining materials;
- Compatibility with the conditions of use;
- Compatibility with the surrounding environment or exposure;
- Toxicity;
- Failure mode;
- Ability to fabricate into the desired form;
- Economics;
- Availability.

## Compatibility with hydrogen

- Hydrogen damage

---

# 2.- Material compatibility with hydrogen



Hydride embrittlement

Hydrogen attack

Blistering

Shatter cracks, flakes, fish-eyes and micro perforations

Porosity

Hydrogen reaction embrittlement

Environmental hydrogen embrittlement

Internal hydrogen embrittlement

Hydrogen embrittlement

**Hydrogen damage**

Low-temperature effects

Thermal contraction

Thermal gradient

Low-temperature embrittlement

## 2.1.- Hydrogen embrittlement

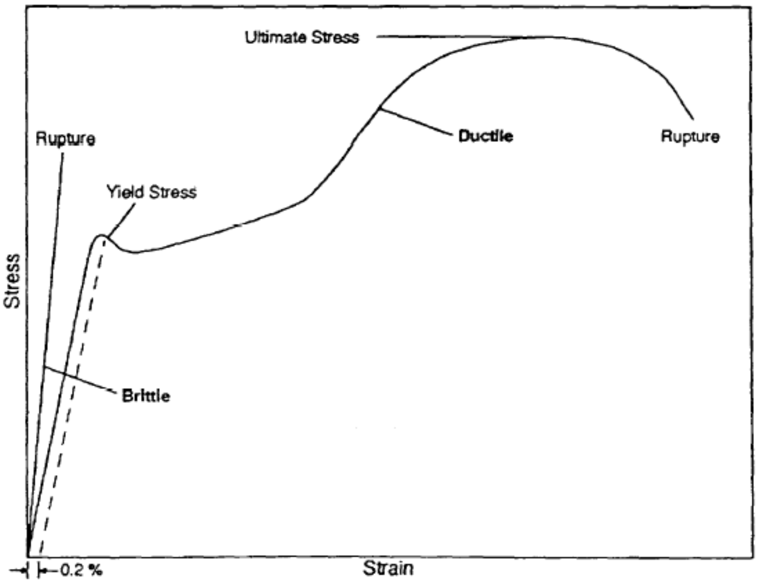
✓ *Some materials can undergo a significant loss of their structural strength when exposed to hydrogen.*

✓ *At temperatures close to ambient a number or metallic materials are suscpetible to hydrogen embrittlement, particularly those with a body-centred cubic crystal lattice structure.*

Phenomena

- Hydrogen reaction embrittlement;
- Internal hydrogen embrittlement;
- Environmental hydrogen embrittlement.

## 2.1.- Hydrogen embrittlement

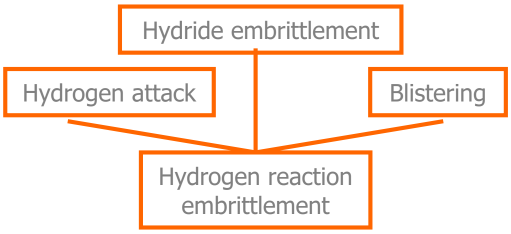


Source: *Hydrogen as an energy carrier and its production by nuclear power,* International Atomic Energy Agency -IAEA-, May 1999.

## 2.1.- Hydrogen embrittlement

### Hydrogen reaction embrittlement

The hydrogen chemically reacts with a constituent of the metal to form a new microstructural element of phase such as a hydride or gas bubbles (“blistering”).



Hydride embrittlement

Hydrogen attack

Blistering

Hydrogen reaction embrittlement

---

## 2.1.- Hydrogen embrittlement

### Hydride embrittlement

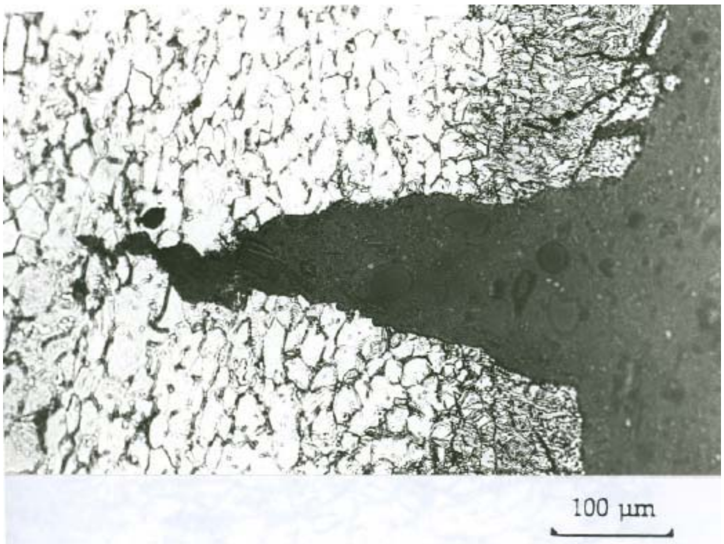
✓ In hydride forming metals like Ti, Zr and V hydrogen absorption causes sever embrittlement.

✓ At low concentrations of hydrogen, below the solid-solubility limit, stress-assisted hydride formation causes the embrittlement which is enhanced by slow straining.

✓ At hydrogen concentrations above the solubility limit, brittle hydrides are precipitated on slip planes and cause severe embrittlement.

*Hydrogen assisted stress corrosion test of Ti Gr-12*

## 2.1.- Hydrogen embrittlement



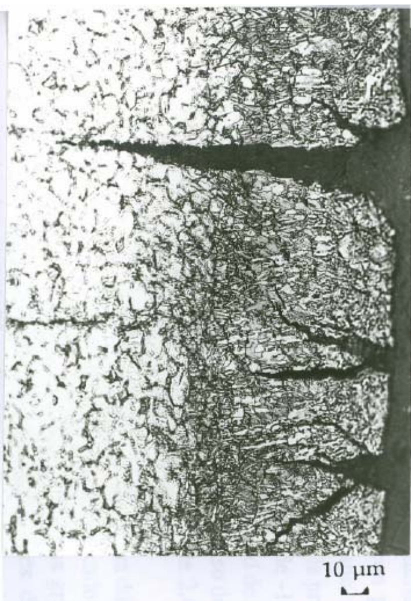
*Hydrogen diffusivity inside the material forming hydrides. Secondary cracks.*

*(Ti GR-12, $2.10^{-7}$ $s^{-1}$ and -1500 V (ECS))*

---

*Hydrogen assisted stress corrosion test of Ti Gr-12*

## 2.1.- Hydrogen embrittlement

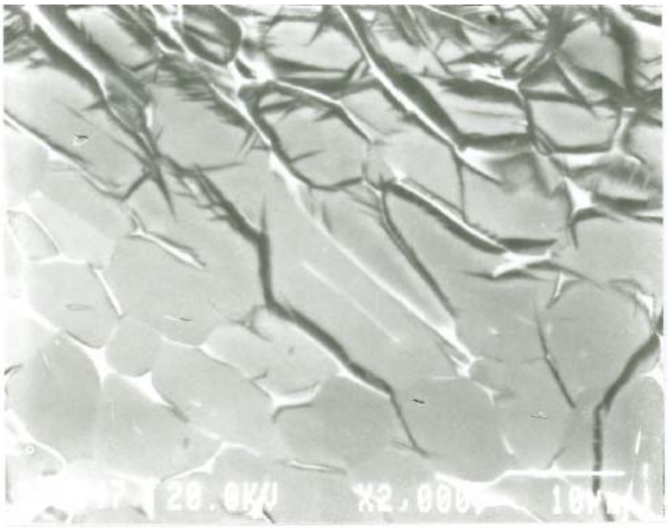


*Hydrogen diffusivity inside the material forming hydrides. Secondary cracks.*

*(Ti GR-12, $2.10^{7}$ s-1 and -1500 V (ECS))*

*Hydrogen assisted corrosion fatigue test of Ti Gr-12*

# 2.1.- Hydrogen embrittlement

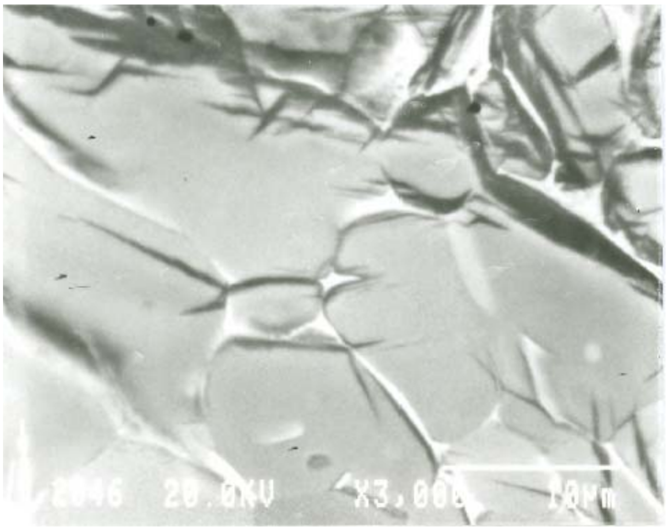


*(Ti Gr-12, 0.2Hz, R=0.7 and -1500mV polarization)*

---

*Hydrogen assisted corrosion fatigue test of Ti Gr-12*

# 2.1.- Hydrogen embrittlement



*(Ti Gr-12, 0.2Hz, R=0.7 and -1500mV polarization)*

## 2.1.- Hydrogen embrittlement

### Blistering

✓ Atomic hydrogen diffusing through metals may collect at internal defects like inclusions and laminations and form molecular hydrogen. High pressures may be built up at such locations due to continued absorption of hydrogen leading to blister formation, growth and eventual bursting of the blister.

### Hydrogen attack

✓ Many low-alloyed structural steels suffer from it at temperatures above 200ºC.

✓ It is a non-reversible degradation of the steel microstructure caused by a chemical reaction between diffusing hydrogen and the carbide particles in the formation of methane.

---

## 2.1.- Hydrogen embrittlement

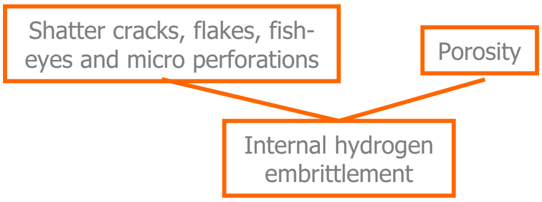
### Internal hydrogen embrittlement

✓ Hydrogen enters the metal during its processing, e.g., chemical reactions with water to form metal oxide and liberate hydrogen.

✓ It is a phenomenon that may lead to the structural failure of material that never has been exposed to hydrogen before.

✓ Internal cracks are initiated showing a discontinuous growth.

✓ The effect is observed in the temperature range between -100 and +100ºC and is most severe near room temperature.



Shatter cracks, flakes, fish-eyes and micro perforations

Porosity

Internal hydrogen embrittlement

## 2.1.- Hydrogen embrittlement

### Shatter cracks, flakes, fish-eyes and micro perforations

✓ Flakes and shatter cracks are internal fissures seen in large forgings. Hydrogen picked up during melting and casting segregates at internal voids and discontinuities and produces these defects during forging.

✓ Fish-eyes are bright patches resembling eyes of fish seen on fracture surfaces, generally of weldments. Hydrogen enters the metal during fusion-welding and produce this defect during subsequent stressing.

✓ Steel containment vessels exposed to extremly high hydrogen pressures develop small fissures or micro perforations through which fluids may leak.

### Porosity

✓ In metals like iron & steel, aluminum and magnesium whose hydrogen solubilities decrease with decreasing temperature, liberation of excess hydrogen during cooling from the melt, (in ingots and castings) produces gas porosity.

---

## 2.1.- Hydrogen embrittlement

### Environmental hydrogen embrittlement

✓ The material is subjected to a hydrogen atmosphere, e.g., storage tanks. Absorbed and/or adsorbed hydrogen modifies the mechanical response of the material without necessarily forming a second phase.

✓ The effect occurs when the amount of hydrogen that is present, is more than the amount that is dissolved in the metal.

✓ The effect strongly depends on the stress imposed on the metal.

✓ It also maximizes at around room temperature.

## 2.1.- Hydrogen embrittlement

### Mechanisms

- New hydrogen-related phases

The formation of hydrides can lead to new hydrogen-related phases which may be brittle and also may have a lower density than the pure metal leading to internal stress.

- Interaction between hydrogen and plastic deformation

The hydrogen distribution in a metal under stress is highly non-uniform which can lead to locally increased hydrogen-enhanced plasticity causing local microscopic deformation and eventually a failure.

- The decohesion theory

The lattice decohesion effect is presumed to cause embrittlement by a decrease in the atomic bonding strength in the presence of hydrogen. A fracture occurs when the stress exceeds the cohesive stress.

---

## 2.1.- Hydrogen embrittlement

- The pressure theory

This theory attributes hydrogen embrittlement to the diffusion of atomic hydrogen into the metal and its accumulation at internal defects. The pressure developed by this precipitation is added to the applied stress and thus lowers the apparent fracture stress. The very high internal pressure enhances void growth and crack propagation. This is true in blister formation but not relevant to cases of reduced ductility or increased rate of crack propagation induced by exposure to low pressure hydrogen. It has also been suggested that dislocation transport could create large internal pressures in voids even when the source of hydrogen was at low fugacities.

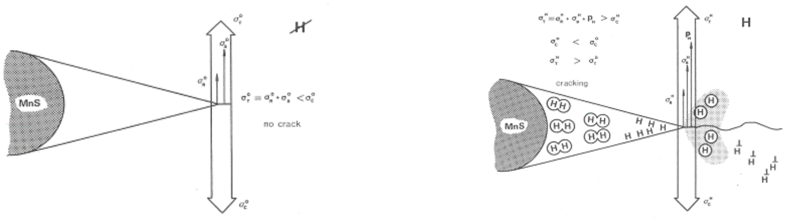
- The surface energy theory

According to this theory hydrogen is adsorbed on the free surface created adjacent to the crack tip decreasing the surface free energy for crack growth.

# 2.1.- Hydrogen embrittlement

- Synthesis

A synthesis of the different current hydrogen embrittlement theory has been suggested by Pressouyre. This is illustrated below. It is assumed that a critical cohesive stress must be exceeded in order to propagate a crack. In the absence of hydrogen, the sum of the stress concentration will be inferior to the cohesive stress, at least for a ductile material under normal service conditions. The presence of hydrogen will have two effects. Firstly, the cohesive stress may be well reduced. Secondly, the total stress may be increased, either by hydrogen effects on the residual stress or by the addition of a hydrogen pressure component.



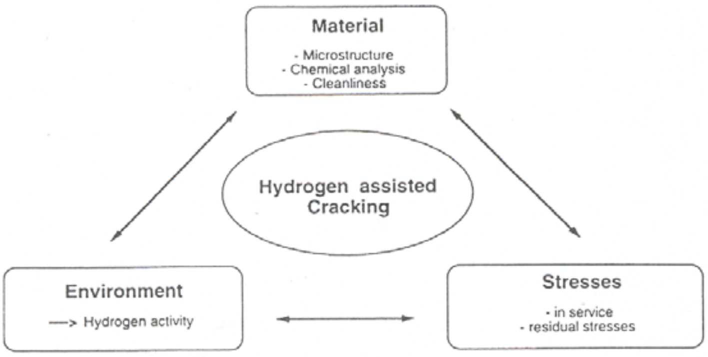
---

# 2.1.- Hydrogen embrittlement

## Susceptibility to hydrogen embrittlement

Necessary conditions for hydrogen embrittlement to occur

- a sensitive material
- an hydrogen supplying environment
- stress level


Material
- Microstructure
- Chemical analysis
- Cleanliness

Hydrogen assisted Cracking

Environment
—> Hydrogen activity

Stresses
- in service
- residual stresses

## 2.1.- Hydrogen embrittlement

Reduction of the susceptibility to hydrogen embrittlement

- ✓ Restricting the hardness, and therefore the strength level of the material used, to a safe value;
- ✓ Lowering the level of applied stress;
- ✓ Minimizing residual stresses;
- ✓ Avoiding or minimizing cold plastic deformation from operations such as cold bending or forming;
- ✓ Avoiding situations that can lead to local fatigue in components that are subjected to frequent load cycles, since hydrogen is known to significantly accelerate a possible initiation and propagation of fatigue cracks in a structure;

---

## 2.1.- Hydrogen embrittlement

- ✓ Using austenitic stainless steels, which in general are less susceptible to hydrogen embrittlement and are commonly used as structural materials for hydrogen equipment because of their excellent toughness behaviour at cryogenic temperatures;
- ✓ Using the test methods specified in ISO 11114-4 to select metallic material resistant to hydrogen embrittlement.

❖The suitability of some commonly used materials for use with hydrogen is shown in the following tables included in the *Technical Report ISO/TR 15916:2004 Basic considerations for the safety of hydrogen systems*, which is provided as a guideline and for informative purposes only.

## 2.1.- Hydrogen embrittlement

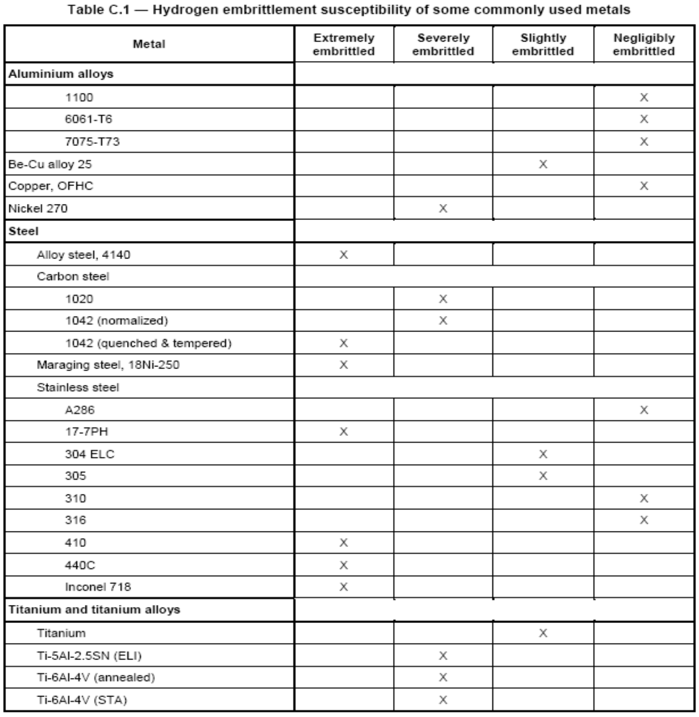


Table C.1 — Hydrogen embrittlement susceptibility of some commonly used metals

| Metal | Extremely embrittled | Severely embrittled | Slightly embrittled | Negligibly embrittled |
|---|---|---|---|---|
| **Aluminium alloys** | | | | |
| 1100 | | | | X |
| 6061-T6 | | | | X |
| 7075-T73 | | | | X |
| Be-Cu alloy 25 | | | X | |
| Copper, OFHC | | | | X |
| Nickel 270 | | X | | |
| **Steel** | | | | |
| Alloy steel, 4140 | X | | | |
| Carbon steel | | | | |
| 1020 | | X | | |
| 1042 (normalized) | | X | | |
| 1042 (quenched & tempered) | X | | | |
| Maraging steel, 18Ni-250 | X | | | |
| Stainless steel | | | | |
| A286 | | | | X |
| 17-7PH | X | | | |
| 304 ELC | | | X | |
| 305 | | | X | |
| 310 | | | | X |
| 316 | | | | X |
| 410 | X | | | |
| 440C | X | | | |
| Inconel 718 | X | | | |
| **Titanium and titanium alloys** | | | | |
| Titanium | | | X | |
| Ti-5Al-2.5SN (ELI) | | X | | |
| Ti-6Al-4V (annealed) | | X | | |
| Ti-6Al-4V (STA) | | X | | |

---

## 2.2.- Low temperature effects

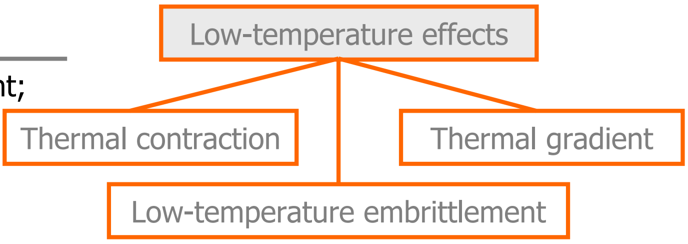
✓ *The choice of a material for use at liquid hydrogen temperature of 20K involves material behaviour considerations such as the following:*

- *Transition from ductile to brittle behaviour as a function of temperature;*
- *Modes of plastic deformation;*
- *Effects of metallurgical instability and phase transformations in the crystalline structure on mechanical and elastic properties.*

✓ *Two of the primary considerations in the selection of a material for liquid hydrogen service are low-temperature ductility (low-temperature embrittlement) and thermal contraction.*

Phenomena

- Low-temperature embrittlement;
- Thermal contraction;
- Thermal gradient.



Low-temperature effects

Thermal contraction

Thermal gradient

Low-temperature embrittlement

# 2.2.- Low temperature effects

## Low-temperature embrittlement

- ✓ Many materials change from ductile to brittle behaviour as their temperature is lowered. This change in behaviour can occur at temperatures much higher than cryogenic temperatures.
- ✓ Generally, a material that has a ductile-to-brittle transition temperature above 20K should not be used with liquid hydrogen.
- ✓ Most polymers become brittle at temperatures much higher than liquid hydrogen temperature.

## Thermal contraction

- ✓ Materials generally have a positive expansion coefficient. The temperature span from ambient to liquid hydrogen temperature is about 280K. Such a large temperature decrease can result in significant thermal contraction in most materials.
- ✓ The thermal expansion coefficient itself is a function of temperature.

---

# 2.2.- Low temperature effects

## Thermal gradient

- ✓ The components of a cryogenic system usually undergo a thermal gradient; some only during cool-down or warm-up phases, others even at steady state of operation.
- ✓ Strong gradients, particularly if non-linear, result in stresses which under certain circumstances my lead to rupture.

## 2.3.- Material suitability for hydrogen service

✓ A material should be evaluated carefully before it is used for hydrogen service.

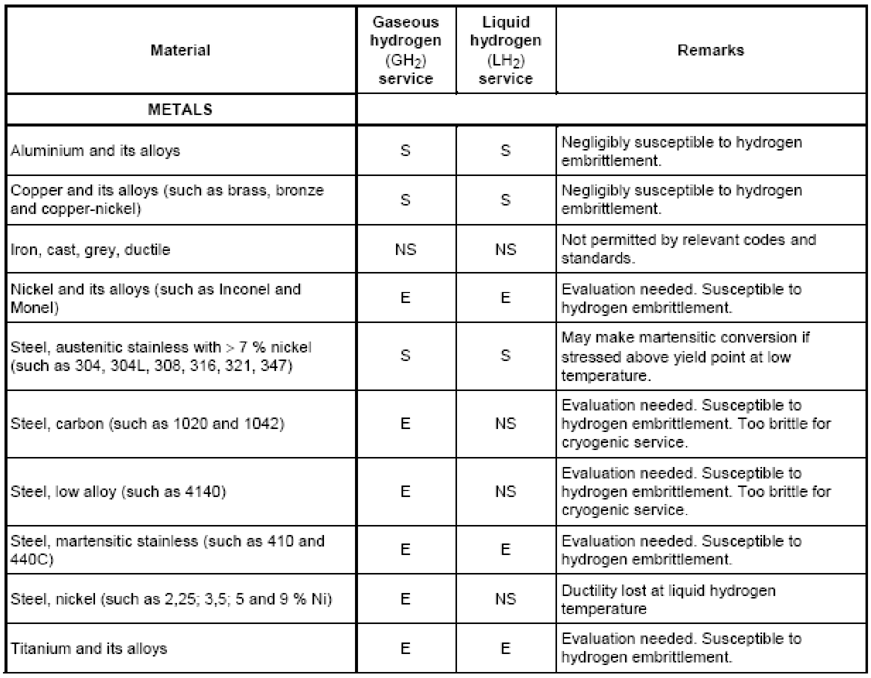
✓ A material should not be used for hydrogen service unless data are available to show that the material is suitable for the intended service conditions.

❖ The suitability of some commonly used materials for use with hydrogen is shown in the following tables included in the *Technical Report ISO/TR 15916:2004 Basic considerations for the safety of hydrogen systems*, which is provided as a guideline and for informative purposes only.

---

## 2.3.- Material suitability for hydrogen service

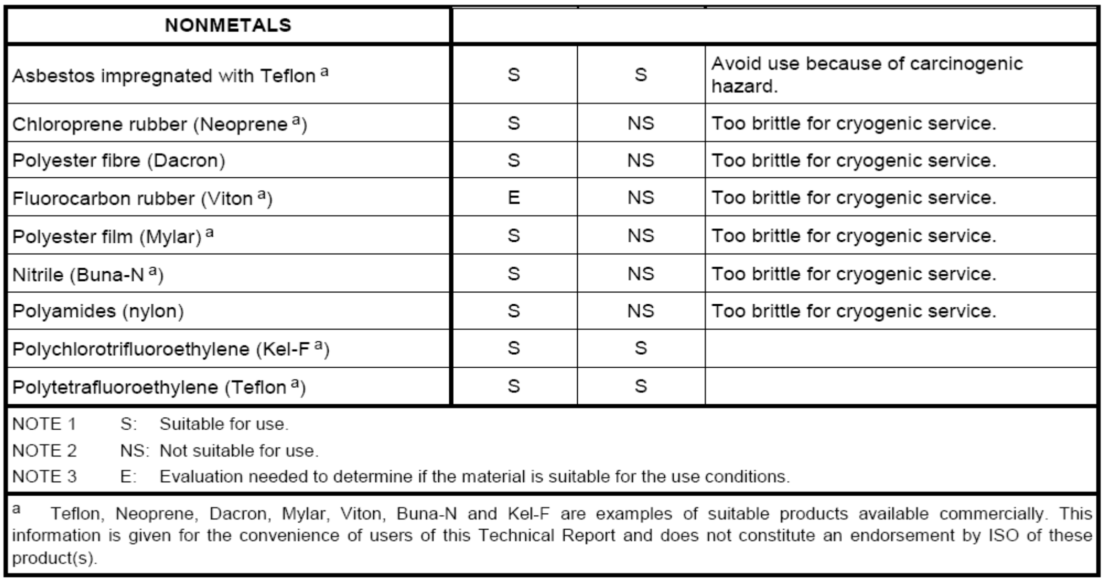
**Table C.2 — Suitability of some selected materials for hydrogen service**



| Material | Gaseous hydrogen ($GH_2$) service | Liquid hydrogen ($LH_2$) service | Remarks |
|---|---|---|---|
| **METALS** | | | |
| Aluminium and its alloys | S | S | Negligibly susceptible to hydrogen embrittlement. |
| Copper and its alloys (such as brass, bronze and copper-nickel) | S | S | Negligibly susceptible to hydrogen embrittlement. |
| Iron, cast, grey, ductile | NS | NS | Not permitted by relevant codes and standards. |
| Nickel and its alloys (such as Inconel and Monel) | E | E | Evaluation needed. Susceptible to hydrogen embrittlement. |
| Steel, austenitic stainless with > 7 % nickel (such as 304, 304L, 308, 316, 321, 347) | S | S | May make martensitic conversion if stressed above yield point at low temperature. |
| Steel, carbon (such as 1020 and 1042) | E | NS | Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service. |
| Steel, low alloy (such as 4140) | E | NS | Evaluation needed. Susceptible to hydrogen embrittlement. Too brittle for cryogenic service. |
| Steel, martensitic stainless (such as 410 and 440C) | E | E | Evaluation needed. Susceptible to hydrogen embrittlement. |
| Steel, nickel (such as 2,25; 3,5; 5 and 9 % Ni) | E | NS | Ductility lost at liquid hydrogen temperature |
| Titanium and its alloys | E | E | Evaluation needed. Susceptible to hydrogen embrittlement. |

## 2.3.- Material suitability for hydrogen service

**Table C.2** (*continued*)



| NONMETALS | | | |
|---|---|---|---|
| Asbestos impregnated with Teflon [a] | S | S | Avoid use because of carcinogenic hazard. |
| Chloroprene rubber (Neoprene [a]) | S | NS | Too brittle for cryogenic service. |
| Polyester fibre (Dacron) | S | NS | Too brittle for cryogenic service. |
| Fluorocarbon rubber (Viton [a]) | E | NS | Too brittle for cryogenic service. |
| Polyester film (Mylar) [a] | S | NS | Too brittle for cryogenic service. |
| Nitrile (Buna-N [a]) | S | NS | Too brittle for cryogenic service. |
| Polyamides (nylon) | S | NS | Too brittle for cryogenic service. |
| Polychlorotrifluoroethylene (Kel-F [a]) | S | S | |
| Polytetrafluoroethylene (Teflon [a]) | S | S | |

NOTE 1 S: Suitable for use.
NOTE 2 NS: Not suitable for use.
NOTE 3 E: Evaluation needed to determine if the material is suitable for the use conditions.

[a] Teflon, Neoprene, Dacron, Mylar, Viton, Buna-N and Kel-F are examples of suitable products available commercially. This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of these product(s).

---

## 2.3.- Material suitability for hydrogen service

### Non-metallic materials: sealants

- ✓ The application of non-metallic materials (rubber or plastic) as sealants has a long history of use in hydrogen service. Most polymers cause no problems in connection with hydrogen. However, hydrogen can diffuse through these materials much more easily than through metals. The amounts usually are not sufficient to create ignitable mixtures outside the vessel, but they can cause a loss of gas over a long period of time, or they could spoil an insulation vacuum.

- ✓ Proper care should be exercised in the selection of organic materials used as sealant for high pressure hydrogen service. The permeation of hydrogen into these materials over an extended period of time, followed by rapid depressurization, can result in mechanical failure of shredding of the seals.

- ✓ Fibre-reinforced polymers (FRP) are becoming more and more important as materials for pressure vessels. A metal liner is usually placed inside the vessel to hold the hydrogen so that the FRP material is no in direct contact with hydrogen.

## 3.- Materials Testing

### ISO Standards

- ISO 2626:1973

*Copper -- Hydrogen embrittlement test*

- ISO 9022-20:1997

*Optics and optical instruments -- Environmental test methods -- Part 20: Humid atmosphere containing sulfur dioxide or hydrogen sulfide*

- *ISO 9587:1999*

*Metallic and other inorganic coatings -- Pretreatments of iron or steel to reduce the risk of hydrogen embrittlement*

- *ISO 9588:1999*

*Metallic and other inorganic coatings -- Post-coating treatments of iron or steel to reduce the risk of hydrogen embrittlement*

---

## 3.- Materials Testing

- ISO 15330:1999

*Fasteners -- Preloading test for the detection of hydrogen embrittlement -- Parallel bearing surface method*

- ISO 17081:2004

*Method of measurement of hydrogen permeation and determination of hydrogen uptake and transport in metals by an electrochemical technique*

## 3.- Materials Testing

- ISO 11114-4:2005

Transportable gas cylinders – Compatibility of cylinder and valve materials with gas contents – Part 4: Test methods for selecting metallic materials resistant to hydrogen embrittlement.

*This part of ISO 11114 specifies test methods and the evaluation of results from these tests in order to qualify steels suitable for use in the manufacture of gas cylinders (up to 3 000 l) for hydrogen and other embrittling gases.*

*This part of ISO 11114 only applies to seamless steel gas cylinders.*

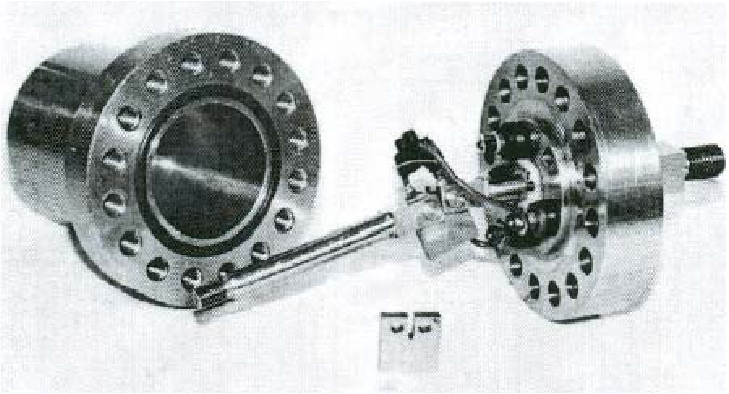
*The requirements of this part of ISO 11114 are not applicable if at least one of the following conditions for the intended gas service is fulfilled:*

*- the working pressure of the filled embrittling gas is less than 20 % of the test pressure of the cylinder;*

*- the partial pressure of the filled embrittling gas of a gas mixture is less than 5 MPa (50 bar) in the case of hydrogen and other embrittling gases, with the exception of hydrogen sulphide and methyl mercaptan in which cases the partial pressure shall not exceed 0,25 MPa (2,5 bar).*

---

## 3.- Materials Testing



*Stainless steel chamber, load bars and test sample.*

# 3.- Materials Testing

## ASTM Standards

- F1940-01

*Standard test method for process control verification to prevent hydrogen embrittlement in plated or coated fasteners*

- F1624-06

*Standard test method for measurement of hydrogen embrittlement threshold in steel by the incremental step loading technique*

- F519-05

*Standard test method for mechanical hydrogen embrittlement evaluation of plating processes and service environments*

---

# 3.- Materials Testing

## NACE Standards

- TM-01-77

*Laboratory testing of metals for resistance to sulfide stress cracking and stress corrosion cracking in $H_2S$ environments*

*This standard covers the testing of metals subjected to tensile stresses for resistance to cracking failure in low-Ph aqueous environments containing H2S. Carbon and lowalloy steels are commonly tested for environmental cracking resistance at room temperature where SSC susceptibility is typically high. For other types of alloys the correlation of environmental cracking susceptibility with temperature is more complicated.*

- TM-02-84

*Standard test method. evaluation of pipeline and pressure vessel steels for resistance to Hydrogen-Induced Cracking*

*This standard establishes a test method for evaluating the resistance of pipeline and pressure vessel plate steels to HIC caused by hydrogen absorption from aqueous sulfide corrosion.*

# 4.- References

- *Stress Corrosion Cracking and Hydrogen embrittlement of Iron Base Alloys. NACE. June 1973.*
- *Corrosión bajo factores mecánicos asistida por hidrógeno de aleaciones de titanio. Tesis doctoral. I. Azkarate. IQS. Barcelona. 1992.*
- *Hydrogen as an energy carrier and its production by nuclear power. International Atomic Energy Agency IAEA TECDOC 1085. K. Verfonderen, May 1999.*
- *State of the Art "Durability & Integrity". CEA contribution (Work Package 3 – Task 3.1) / Naturalhy FP6-502661. Foulc M.P., Mazabraud P. and Farys C. of -CEA-, Coudreuse L. of Industeel Arcelor and Olmedo L.*
- *Hydrogen embrittlement in power plant steels, Dayal R.K. and Parvathavarthini N. of Indira Gandhi Centre for Atomic Research, Kalpakkam India, Sadhana Vol.28, Parts 3&4, June/August 2003, pp 431-451.*
- *Basic considerations for the safety of hydrogen systems, Technical report ISO/TR 15916:2004.*
- *Hydrogen Safety Course, Materials and Hydrogen. Marmara Research Center. TUBITAK. 6th June 2006. I. Azkarate, TECNALiA-INASMET. Lionel Perrete INERIS.*