# GASEOUS HYDROGEN REFUELING STATIONS: SELECTION OF MATERIALS FOR HIGH PRESSURE HYDROGEN FUELING CONNECTORS

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**ABSTRACT**

Design of hydrogen fueling components is critical for safety and reliability. Intensive usage of such components in urban public environment is expected in the near future. Any leakage of gas or failure of equipment will create potential hazards. Materials for such category of equipment must have specific mechanical characteristics, including hardness (influence on the durability of the equipment and on the resistance to hydrogen) and be easy to machine. Air Liquide has developed a test program for qualifying equipment representing the present state of the art. Studies on the susceptibility of various steels to hydrogen embrittlement have been done. Test specimens were exposed to static and cyclic loads with hydrogen and an inert gas, the inert gas representing a reference. Various tests are described here. As a result, the importance of further development in the design and selection of appropriate materials for critical hydrogen components is required. Various options are presented and discussed.

## 1.0 INTRODUCTION

The components used for the dispensing line of a hydrogen fueling station are very critical for safety and reliability (see fig. 1). This is particularly true for the quick connectors used at 350 or 700 bars. The field experience of such equipment is, of course, very limited and their operational conditions and duties are to be further considered.


Figure 1. Example of fueling station for hydrogen vehicles

One of the most critical aspects is to ensure the hydrogen compatibility of the materials used for the construction of such equipment.

Non-metallic materials are used to provide the adequate tightness and the selection of appropriate plastics and elastomers is a real challenge considering hydrogen fluidity, cyclic stresses during repeated fillings, aging for materials and wide operating temperature range (from – 50°C to + 80°C or more).

Another challenge is the selection of metallic materials not susceptible to hydrogen embrittlement. This aspect is treated in this paper.

## 2.0 HYDROGEN EMBRITTLEMENT

The phenomenon of "internal hydrogen embrittlement" due to excessive amounts of hydrogen introduced during the manufacture of steels has been known since the end of the 19$^{th}$ century. The phenomenon of internal hydrogen embrittlement when welding steels was discovered later. These two phenomena are now well mastered and are not covered here. This paper only concerns the phenomenon of "external hydrogen embrittlement" caused by gaseous hydrogen under pressure in contact with steels. The hydrogen penetrates into the steel (during operation in the case of pressurized vessels) and diminishes local or overall mechanical properties of steel. This can lead to the bursting of these pressurized vessels under certain conditions.

The hydrogen which penetrates into steels can be found either in metallic solution or in a combined state ($H_2$, $CH_4$ molecules).

When hydrogen is found in metallic solution, the phenomenon of steel deterioration is called "gaseous hydrogen embrittlement" ; this phenomenon generally takes place at temperatures close to ambient , and the penetration or transport of the hydrogen takes place essentially by "transport by dislocations" when the material is undergoing deformation ; this phenomenon thus occurs essentially in areas with local plastic deformations.

When hydrogen is found in a combined state, it is a matter of "hydrogen attack". The hydrogen reacts with the carbon in the steel to form molecules of methane ; this leads to the formation of micro-cavities in the steel and to a reduction of carbon in the steel, which leads to a reduction in the overall strength of the material. Hydrogen is thus "transported" by diffusion. This phenomenon mainly takes place at high temperature. In addition, contrary to the phenomenon of hydrogen embrittlement, this phenomenon is only reversible as long as micro-cavities have not yet formed.

One of the most important parameters to be considered is temperature. Indeed, hydrogen embrittlement in steels occurs mainly around ambient temperature and tends to disappear at high temperature. On the other hand, "hydrogen attack" only takes place at high temperature. Depending on whether the operating temperature is higher or lower than 200°C, one or the other of the two phenomena mentioned above should be considered. In the case of fueling stations, hydrogen embrittlement is thus the only concern.

The parameters to be considered are:

- "environmental"
- "material"
- design and quality of manufacture (surface condition).

We only consider the material parameters in this paper. Material parameters can be grouped into two categories, according to whether their effect:

- Modifies the "trapping" of hydrogen, which in turn affects the critical concentration of hydrogen in the material; this traps can be inclusions, particles, grain boundaries, dislocations and pre existing defects ; or

- Modifies the behaviour of the "surroundings of the traps" (microstructure, chemical composition, mechanical properties).

In a practical way, the effect of these parameters can be checked with disk bursting tests (see [2]), to select materials resistant to hydrogen embrittlement phenomena.

The microstructure of steels (resulting from chemical composition and heat treatment) plays an essential role in Hydrogen Embrittlement behaviour. It is recognized that martensitic structures have the worst behaviour, ferritic structures an intermediate behaviour, and stable austenitic steels exhibit the best behaviour.

In the case of fueling connectors, two specific parameters need to be considered:

- The service conditions and, in particular the fatigue phenomena created by the repetitive filling cycles; it is well known that hydrogen reduces the life by accelerating the crack propagation during fatigue cycles

- The use of some materials which may not be "hydrogen compatible". The springs are made of high strength materials (such as cold worked stainless steels) ; other parts subjected to friction (and displacement) must be hard enough to withstand the service condition. Such high strength materials are normally very sensitive to hydrogen embrittlement.

## 3. HYDROGEN EMBRITTLEMENT – TEST METHODS

Different types of test methods can be used [1]:

- "Static" methods (delayed rupture test)

- Or "dynamic" methods which are either conducted under constant strain rate or under cyclic stresses (fatigue tests).

In the investigation of HE, dynamic methods shall be preferred considering as indicated before the "hydrogen transport" by dislocations phenomenon. The different tests specimens that can be used are:

- Fracture mechanic specimen (CT WOL specimens) (fig. 2)

- Tensile test specimen (fig. 3) [4]

- Disk test specimen

- Other mechanical test specimen (semi-finished products).

Other test methods can be used to evaluate hydrogen permeation and "trapping" but not directly the hydrogen embrittlement effect.

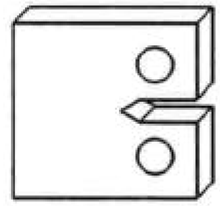


Figure 2. Specimens for compact tension test

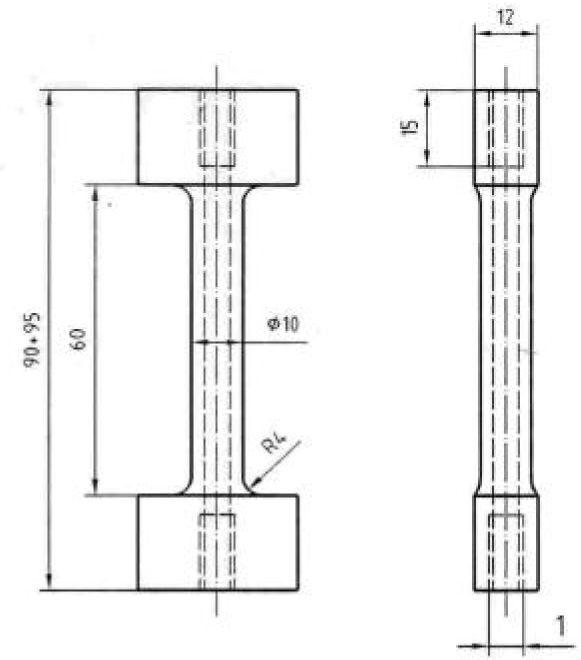



Figure 3. Tensile specimen for hydrogen tests (hollow tensile specimen) (can also be performed with specimens cathodically charged or with tensile specimens in a high pressure cell)

In the case of methods making used of tensile specimens, they can be exposed to high pressure hydrogen or cathodically charged ("F % test"). In both cases, there is not a significant variation of the tensile strength of the material due to the hydrogen charging. The hydrogen effect is measured by the fact that very sensitive materials failed with no "reduction of area". An embrittlement index can be defined as follow:

$I = (\% RA_N - \% RA_H) / \% RA_N$ , with:

$I$ = embrittlement index. $RA_N$ = reduction of area without $H_2$. $RA_H$ = Reduction of area without $H_2$

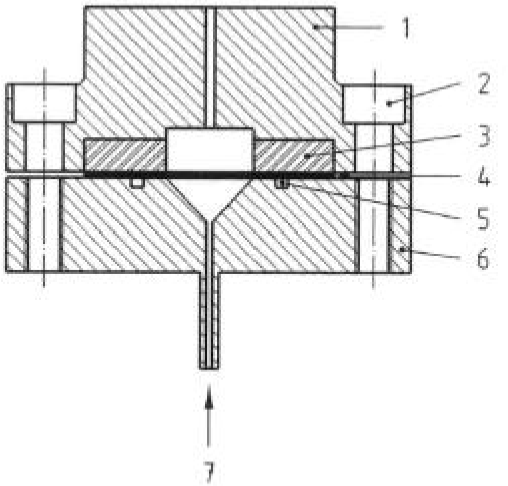
The disk test method is probably the most appropriate to investigate HE.

The principle [2]: a mounted test piece in the shape of a disk is subjected to an increasing gas pressure at constant rate to burst or to crack. The embrittling effect of hydrogen is evidenced by comparing the hydrogen rupture pressure $P_{H2}$ with the helium rupture pressures $P_{He}$, helium being chosen as a reference gas. The ration $P_{He}/P_{H2}$ shall be determined. The lower this ratio, the better will the steel type behave in the presence of hydrogen. This ratio is dependent on the pressure rise rate, which shall remain constant during the whole test.

Note 1: Hydrogen rupture pressures also depend on the hydrogen purity. Oxygen or traces of water vapour can partially inhibit the hydrogen embrittlement effect.

Note 2: The test can be carried out with any other embrittling gas or gas mixtures (e.g. $H_2S$, hydrides). The embrittlement index of the considered gas will then be defined similarly.

Fig.4 shows the cell with the disk sample.




1. Upper flange
2. Bolt hole
3. High-strength steel ring
4. Disk
5. O-ring
6. Lower flange
7. Gas inlet

Figure 4. Disk testing method – Rupture cell for embedded disk-specimen

Fig. 5 gives the principle (test curves) and shows how the embrittlement index is defined.

On fig. 6, test run on "reference" materials explains why a material with an index of 2 (or less) must be used.

With disk samples, pressure fatigue tests can also be performed (see fig. 7 and fig. 8). An example of fatigue tests (under $H_2$ and $N_2$) are given on fig. 9. Fig. 10 also shows how to detect crack initiation when performing fatigue test with disk samples.

A full study was sponsored by the European Commission some years ago [1]. The conclusion is summarized in the tables 1, 2 and 3.

It was concluded that the disk test is the most appropriate test to study HE in metallic materials. The main advantages are:

- Its represents true HE phenomenon ("external" $H_2$ and "transport by dislocation")
- The disk specimen and associated cell are small and very simple (this means in particular that the specimen can be easily taken from the finished materials and the cell is easy to clean (easy removal of small traces of oxygen and $H_2O$ vapour)
- The method has a high sensitivity, makes it possible to rank the materials and to define a criterion (maximum HE index) for the selection of the hydrogen compatible materials.

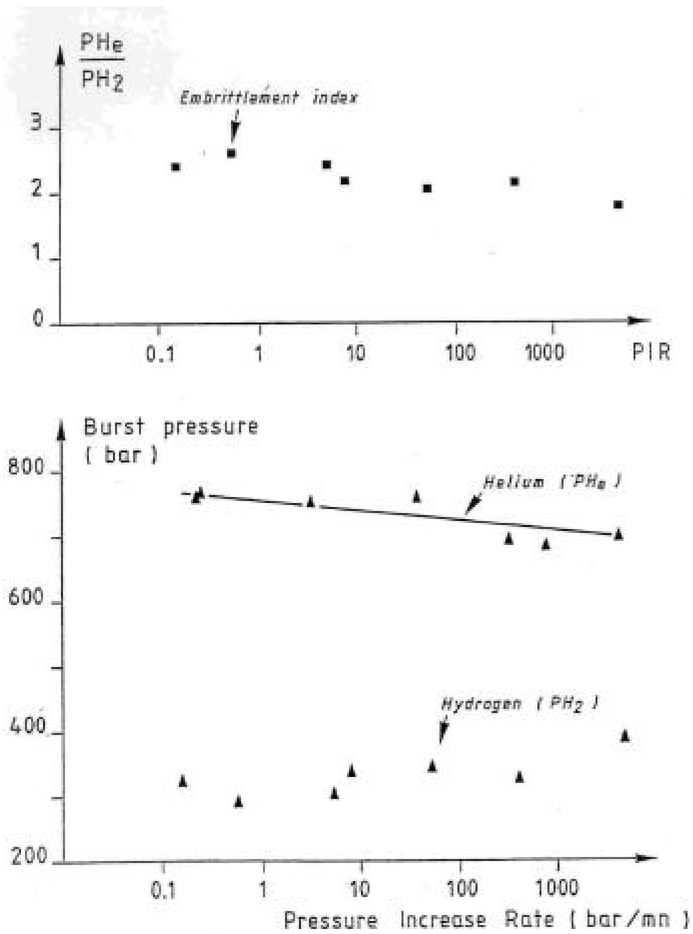
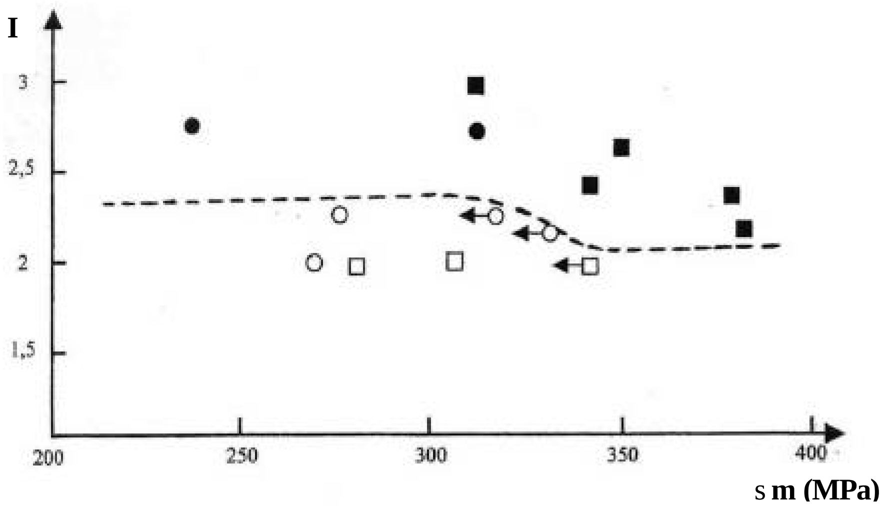



Figure 5. Example of a disk rupture test curve




? Thin wall cylinders - ? Thick wall cylinders (Good $H_2$ behaviour)
■ Thin wall cylinders - ● Thick wall cylinders (Bad $H_2$ behaviour)

Figure 6. Hydrogen embrittlement indexes (I) of reference materials versus maximum wall stresses (σm) of the corresponding pressure vessels

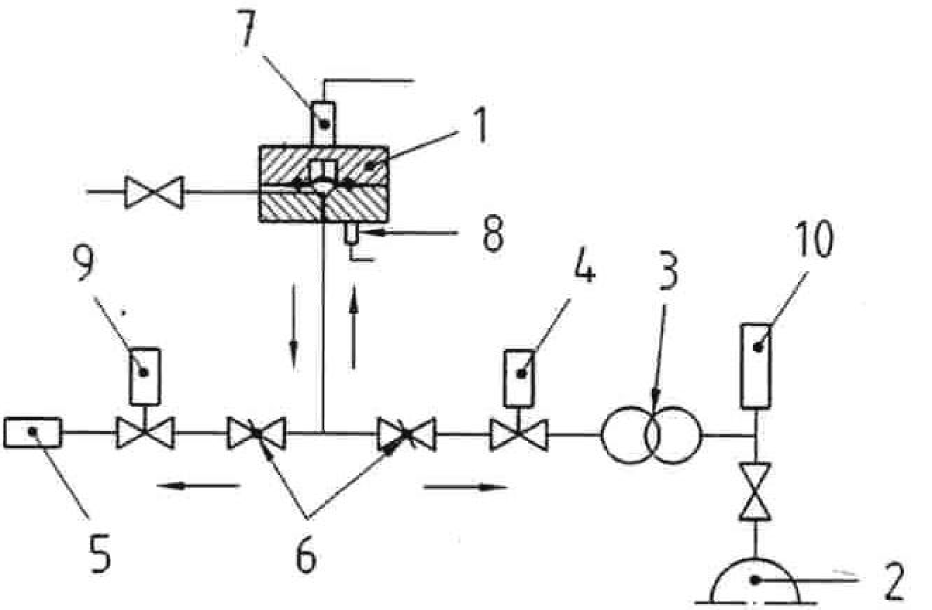



Figure 7. Fatigue test – Principle

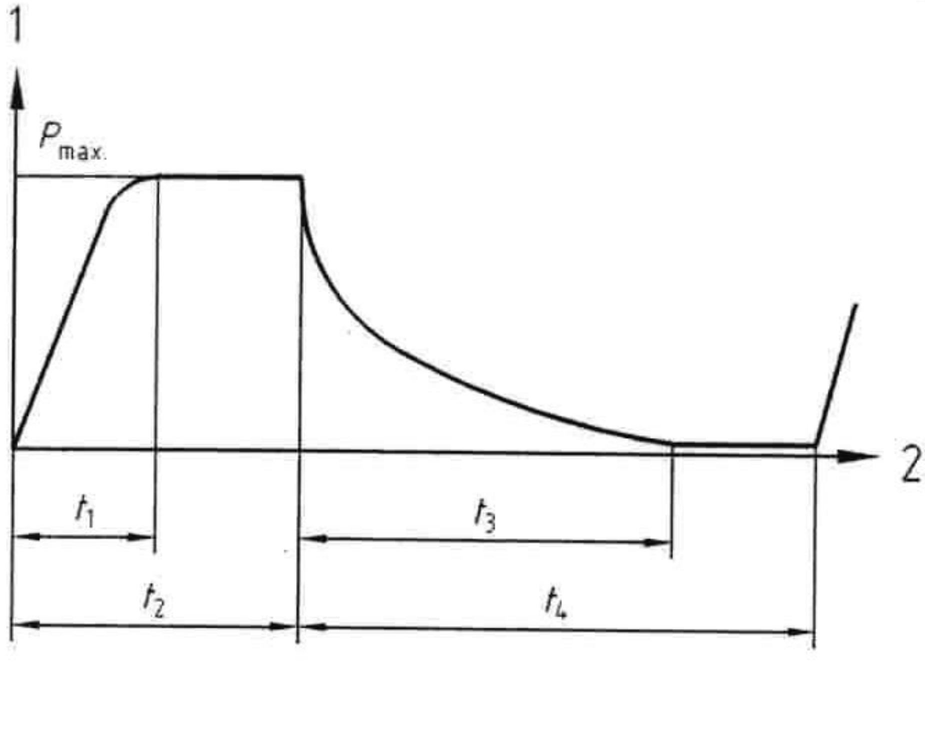



Figure 8. Fatigue test – Pressure cycle

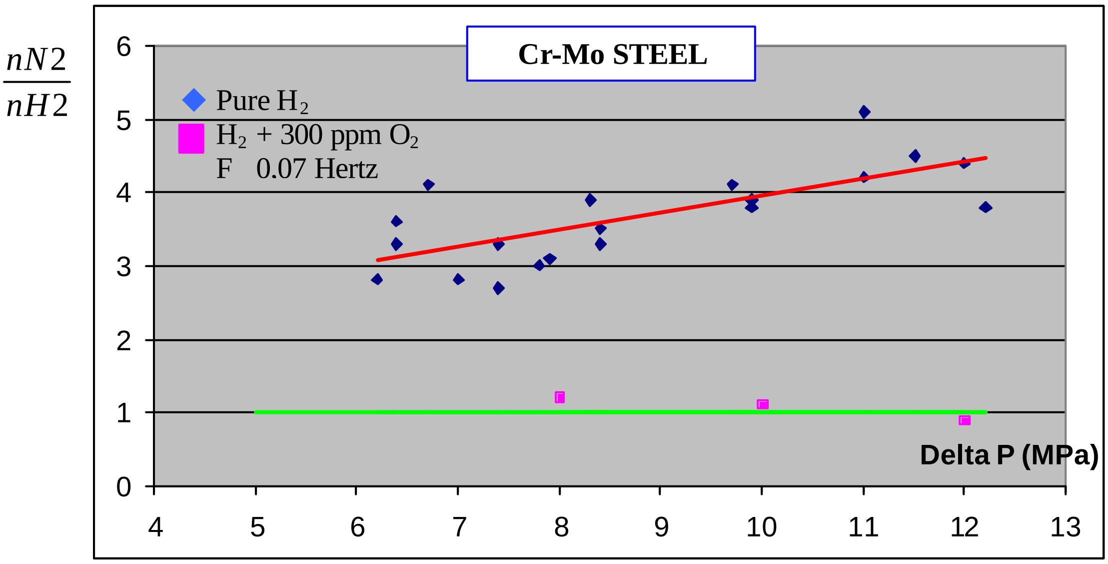



Figure 9. Fatigue tests, $\frac{nN2}{nH2}$ versus $\Delta$ P curves

With $nN_2$ and $nH_2$ respectively number of cycles to failure under $N_2$ and $H_2$

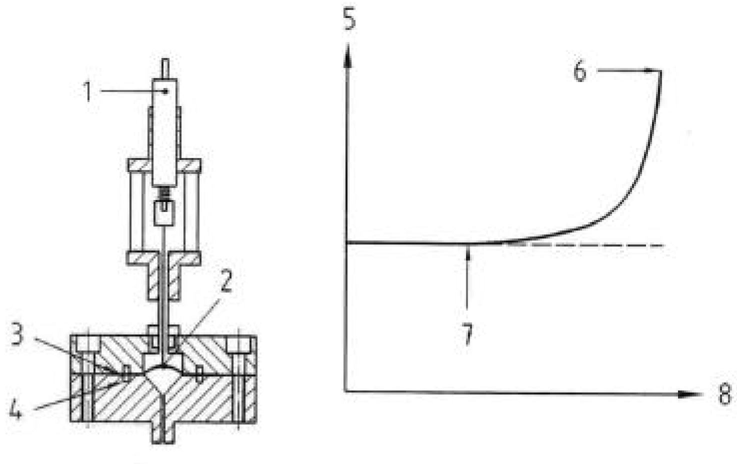



Figure 10. Fatigue test – Principle to detect fatigue crack initiation

Table 1. Tests characteristics. Type of hydrogen embrittlement and transport mode

| Tests | Location of hydrogen | Transport mode |
|---|---|---|
| Disk rupture test | External | Dislocations |
| F % test | External + Internal | Diffusion + Dislocation |
| Hollow tensile specimen test | External | Dislocations |
| Fracture mechanics tests | External | Dislocations |
| P.E.S. test | External | Dislocations |
| Tubular specimen | External | Dislocations |
| Cathodic charging test | External | Diffusion |

Table 2. Tests characteristics. Practical point of view

| Tests | Specimen (Size-complexity) | Cell (Size-complexity) | Complementary equipment needed |
|---|---|---|---|
| Disk rupture test | Small size and very simple | Small size and very simple | Hydrogen compressor and high pressure vessel |
| Tensile test | Relatively small size | Large size | Tensile machine |
| Fracture mechanics test | Relatively large size and complex | Very large size and complex | Fatigue tensile machine for fatigue test only |
| P.E.S. test | Average size and very easy to take from a pipeline | Average size | -- |
| Tubular specimen test | Large size and complex | No cell necessary | Large hydrogen source at high pressure |
| Cathodic charging | Small size and simple | Small size and very simple | Electrochemical equipment (potentiostat) |

Table 3. Tests characteristics. Type of hydrogen embrittlement and transport mode

| Tests | Tests sensibility | Hydrogen behaviour of materials. Possibility of classification | Selection of materials. Existing criteria | Practical data to predict in service performance |
|---|---|---|---|---|
| Disk rupture test | High sensitivity | Possible | Yes $P_{He}/P_{H2}$ | Fatigue life |
| Tensile test | Good/Poor sensitivity | Possible/Difficult | Yes/No | Treshold stress |
| Fracture mechanics | Good sensitivity | Possible | No, but maximum allowable $K_{IH}$ could be defined | - $K_{IH}$<br>- Crack growth rate |
| P.E.S. test | Poor sensitivity | Difficult | No | |
| Tubular specimen test | Good sensitivity | Difficult | No | - $K_{IH}$ |
| Cathodic charging | Good sensitivity | Possible but difficult in practice | No | Critical hydrogen concentration |

## 4. TEST RESULTS

Stainless steels and other high alloy steels are commonly used for fueling connectors. The disk test method (as described before) has been used to study the behaviour of such materials.

Considering stainless steels, our results were published previously [3].

On table 4 are summarized the results of this investigation.

Table 4. Test results

| Main characteristics and embrittlement indexes (E.I.) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| N° | AISI grade | E.I. | Δ | D* (%) | Ni.eq. (%) | MS (°C) | Y.s. (MPa) | u.t.s. (MPa) |
| 1 | 321 | 3.9 | - 1.8 | 12 | 10.25 | - 135 | 280 | 680 |
| 2 | 304 | 2.6 | - 2.2 | 37 | 9.545 | - 168 | 301 | 698 |
| 3 | 304 L | 1.25 | - 1 | 60 | 10.025 | - 150 | 258 | 618 |
| 4 | 316 Ti | 1.3 | + 1.5 | > 100 | 13.25 | - 258 | 299 | 956 |
| 5 | 204 LN | 4.94 | - 4 | 5 | 8.195 | - 232 | 585 | 931 |
| 6 | 304 | 2.13 | - 1 | 30 | 10.97 | - 189 | 343 | 666 |
| 7 | 316 L | 1.29 | + 1.1 | > 100 | 12.88 | - 286 | 278 | 610 |
| 9 | 321 | 3.77 | - 1.9 | 10 | 10.395 | 94 | 254 | 640 |
| 13 | 321 | 5.18 | - 2.2 | 2 | 9.725 | - 129 | 273 | 708 |
| 14 | 301 LN | 4.55 | - 4.2 | 14 | 8.11 | - 224 | 361 | 794 |
| 16 | 316 LN | 1.36 | + 0.6 | > 100 | 12.585 | - 395 | 368 | 703 |
| 17 | 321 | 2.2 | - 0.4 | 30 | 12.11 | - 173 | 264 | 620 |
| 18 | 304 L | 1.2 | + 0.05 | | 12.055 | - 248 | | 583 |
| * Deformation necessary at 20°C to initiate 1 % of martensite formation | | | | | | | | |

Ni.eq. : equivalent nickel
MS : martensite starting temperature
y.s. : yield stress
u.t.s. : ultimate tensile strength

On fig. 11, are summarized the main results.

It shows that, to present a good hydrogen behaviour, a steel needs to have a good stability and a positive delta (Δ), as defined in fig. 11.

When a stainless steel is not stable, it forms martensite after cold working. A martensite structure has the benefit to present a high strength (such structure is commonly used to make good springs or parts needing resistance to friction).

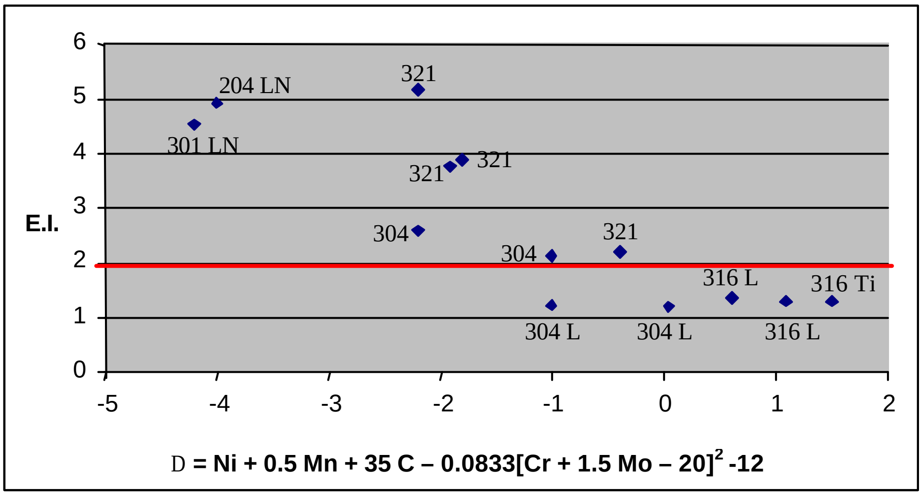



Figure 11. Effect of steel stability (Δ) on the embrittlement index (E.I.)

In table 5, we can see that AISI 316 L has better HE resistance even after formation of martensite. Contrary to AISI 304 or 304 L, AISI 316 L still presents an acceptable hydrogen index (1.71) after formation of a high percentage of martensite.

Table 5. Effect of martensite formed at low temperature and chemical composition

| Steel N° | AISI grade | E.I. | E.I. (20 % MS)* |
|---|---|---|---|
| 3 | 304 | 1.25 | 3.83 |
| 7 | 316 L | 1.29 | 1.71 |
| 18 | 304 L | 1.2 | 3.5 |
| * Embrittlement index after cold working at – 196°C so as to form 20 % martensite in the austenitic structure | | | |

In addition to stainless steel, ferritic or martensitic high alloy steels can be used. Such steels normally contain a high percentage of chromium and a low percentage of nickel.

In fig. 12, are given the test results obtained by the disk test for such a steels.

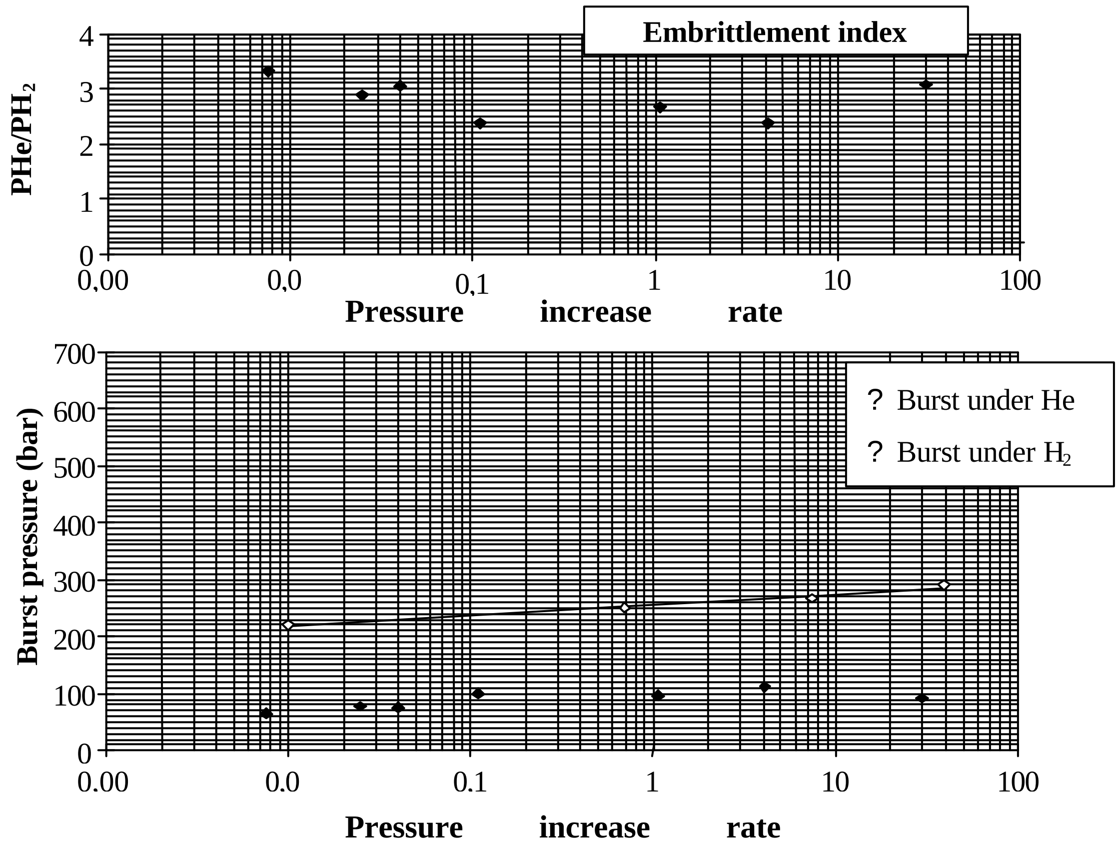



Figure 12. Test results for a 1.4057 (x 7 CrNi 16-2) steel (HV ~ 500 HV)

As shown, the hydrogen embrittlement index is far too high (3.32) to make this steel “hydrogen compatible”.

## 5. SELECTION OF MATERIALS FOR FUELING CONNECTORS

For parts exposed to high pressure hydrogen, only "hydrogen compatible" (as defined before) material is recommended for use.

Non hydrogen compatible materials may only be used:

- If the material is not exposed to hydrogen
- If the material is used at a low enough stress (below a certain stress, failure by hydrogen embrittlement cannot occur)
- If a risk analysis shows that the failure of the hydrogen non compatible material has no consequence on the safe use of the full fueling system
- If the connector is only used for a short period and if fatigue tests performed under hydrogen embrittlement shows that the exposure of the connector to the expected number of cycles during use is safe and acceptable.

## 6 CONCLUSION

In this paper, we have considered a critical part for the dispensing line of an hydrogen fueling station: the fueling connector.

This equipment is exposed during service to very severe conditions. The selection of the right metallic material for such equipment is a real challenge.

We have indicated how to select the right materials by recommending appropriate test methods and design considerations.

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