SECOND JOINT EUROPEAN SUMMER SCHOOL FOR FUEL CELL AND HYDROGEN TECHNOLOGY

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HYDROGEN STORAGE TECHNOLOGIES: COMPATIBILITY OF METALLIC MATERIALS

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HYDROGEN STORAGE TECHNOLOGIES: COMPATIBILITY OF METALLIC MATERIALS WITH HYDROGEN

AIR LIQUIDE

1. **GENERALITIES**

2. **HYDROGEN EMBRITTLEMENT - GENERALITIES**

3. **REPORTED ACCIDENTS AND INCIDENTS ON HYDROGEN EMBRITTLEMENT**

4. **TEST METHODS**

AIR LIQUIDE

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5.1. Environmental parameters

5.2. Design and surface conditions

5.3. Materials

6. HYDROGEN EMBRITTLEMENT OF OTHER MATERIALS

7. HYDROGEN ATTACK

8. CONCLUSION - RECOMMENDATION

1. GENERALITIES

- **Compatibilty between a gas and metallic materials is affected by chemical reactions and physical influences classified into five categories:**

  1.1. Corrosion (the most frequent type of expected reaction)

  1.2. Hydrogen embrittlement

  1.3. Generation of dangerous products through chemical reaction

  1.4. Violent reactions (like ignition)

  1.5. Embrittlement at low temperature

1.1. Corrosion

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a) Dry corrosion

- Is the chemical attack by a dry gas on the cylinder material. The result is a reduction of the cylinder wall thickness. This type of corrosion is not very common, because the rate of dry corrosion is very low at ambient temperature
- At high temperature, hydrogen can react with some materials and can form for example hydrides

1.1. Corrosion

b) Wet corrosion

Most common sources of water ingress:

- **By the customer (retro-diffusion/backfilling or when the cylinder is empty, by air entry, if the valve is not closed)**
- **During hydraulic testing**
- **During filling**

1.1. Corrosion

b) Wet corrosion

Different types of "wet corrosion" in alloys:

- **General corrosion: e.g. by acid gases (CO_2, SO_2) or oxidizing gases (O_2, Cl_2). Additionally some gases, even inert ones, when hydrolysed could lead to the production of corrosive products (e.g. SiH_2Cl_2)**
- **Localised corrosion: e.g. pitting corrosion by wet HCl in aluminium alloys or stress corrosion cracking of highly stressed steels by wet CO/CO_2 mixtures**
- **H_2 cannot even in wet conditions create such types of corrosion**

c) Corrosion by impurities

Most common polluants:

- **Atmospheric air, in this case the harmful impurities can be moisture and oxygen (e.g. in liquefied ammonia)**

- **Agressive products contained in some gases, e.g. H_2S in natural gas**

1.1. Corrosion

c) Corrosion by impurities

- **Agressive traces (acid, mercury, etc.) remaining from the manufacturing process of some gases**

For example, some electrolytic hydrogen can contain traces of mercury (from the diaphragm). Mercury reacts with many metals at room temperature especially aluminium

1.2. Hydrogen embrittlement

- Embrittlement by dry gas can occur at ambient temperature in the case of certain gases and under service conditions with stresses the cylinder material. The best know example is embrittlement caused by hydrogen
- The type of stress cracking phenomenon can, under certain conditions, lead to the failure of gas cylinders (or other metallic components) containing hydrogen, hydrogen mixtures and hydrogen bearing compounds including hydrides

1.2. Hydrogen embrittlement

- **The risk of hydrogen embrittlement only occurs if the partial pressure of the gas and the stress level of the cylinder material is high enough**

- **This compatibility issue is one of the most important and well described in details in the following**

1.3. Generation of dangerous products

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- **In some cases, reactions of a gas with a metallic material can lead to the generation of dangerous products. Examples are the possible reaction of C_2H_2 with copper alloys containing more than 70 % copper and of CH_3Cl in aluminium cylinders**
- **No case known with hydrogen**

1.4. Violent reactions (e.g. ignition)

- **In principle, such types of gas/metallic material reactions are not very common at ambient temperatures, because high activation energies are necessary to initiate such reactions. In the case of some non-metallic materials, this type of reaction can occur with some gases (e.g. O_2, Cl_2)**

1.5. Embrittlement at low temperature

- **Ferritic steels are known to be sensitive to this phenomenon**

- **Liquid hydrogen is very cold (20 K). In such cases, materials having good impact behaviour at low temperature (aluminium alloys, austenitic stainless steels) shall be used and carbon or low alloyed steels shall be rejected**

2. HYDROGEN EMBRITTLEMENT - GENERALITIES

- **Internal hydrogen embrittlement**
- **External hydrogen embrittlement**

2. HYDROGEN EMBRITTLEMENT - GENERALITIES

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1 - COMBINED STATE :

Hydrogen attack

2 - IN METALLIC SOLUTION :

Gaseous hydrogen embrittlement

2. HYDROGEN EMBRITTLEMENT - GENERALITIES

- **Important parameter : THE TEMPERATURE**

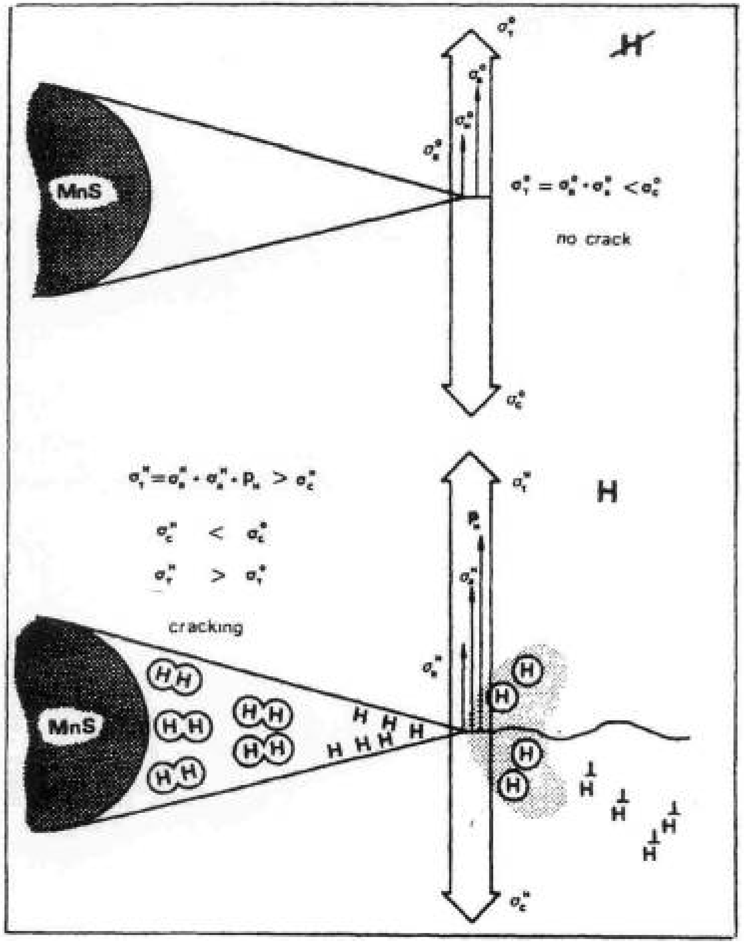
T < 200°C → **Hydrogen embrittlement**

T ≥ 200°C → **Hydrogen attack**

2. HYDROGEN EMBRITTLEMENT - GENERALITIES

- Reversible phenomena
- Transport of H_2 by the dislocations
- H_2 traps

CRITICAL CONCENTRATION AND DECOHESION ENERGY



3. REPORTED ACCIDENTS AND INCIDENTS ON HYDROGEN EMBRITTLEMENT

FAILURE OF A HYDROGEN TRANSPORT VESSEL IN 1980

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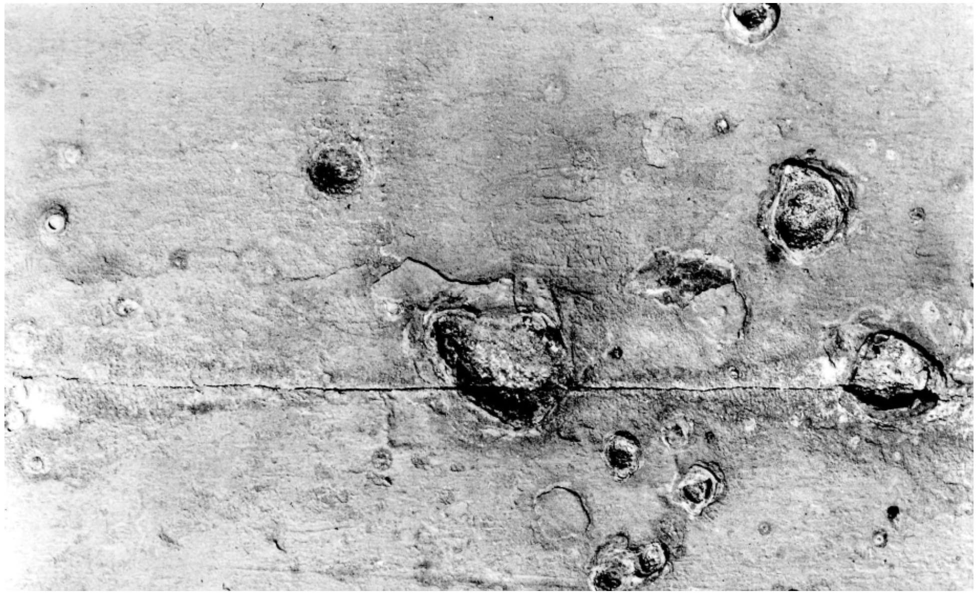

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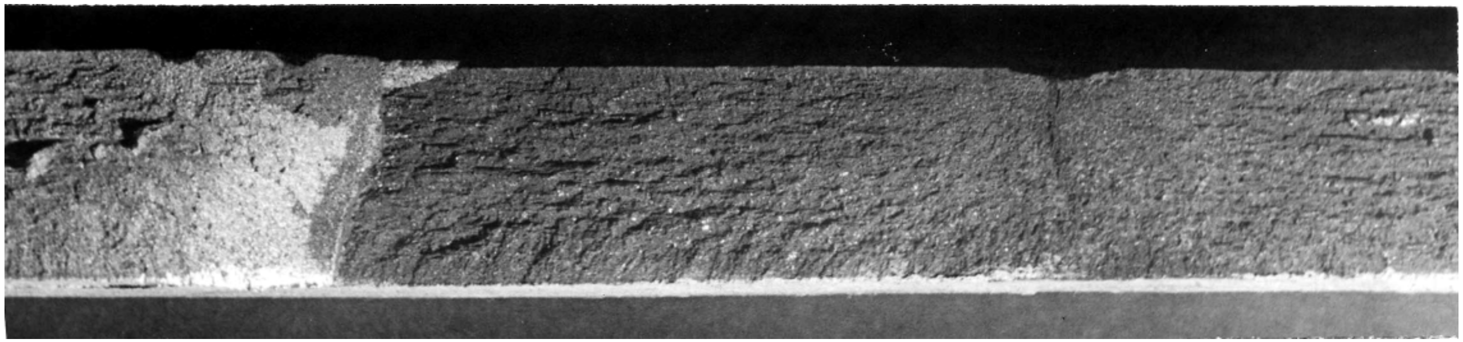

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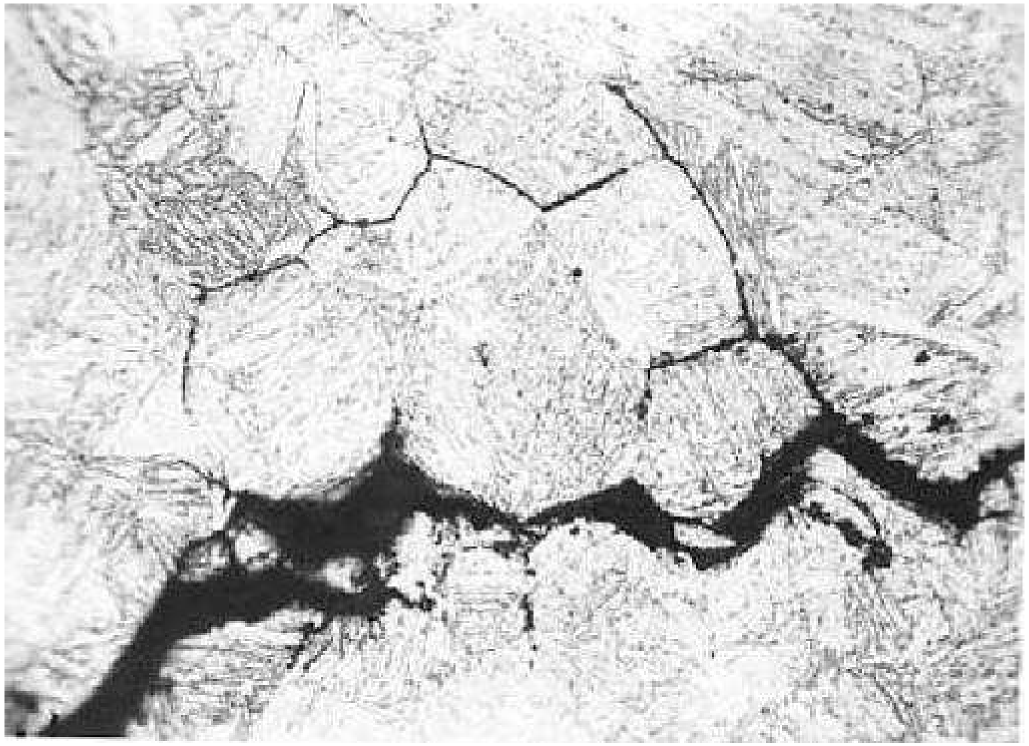


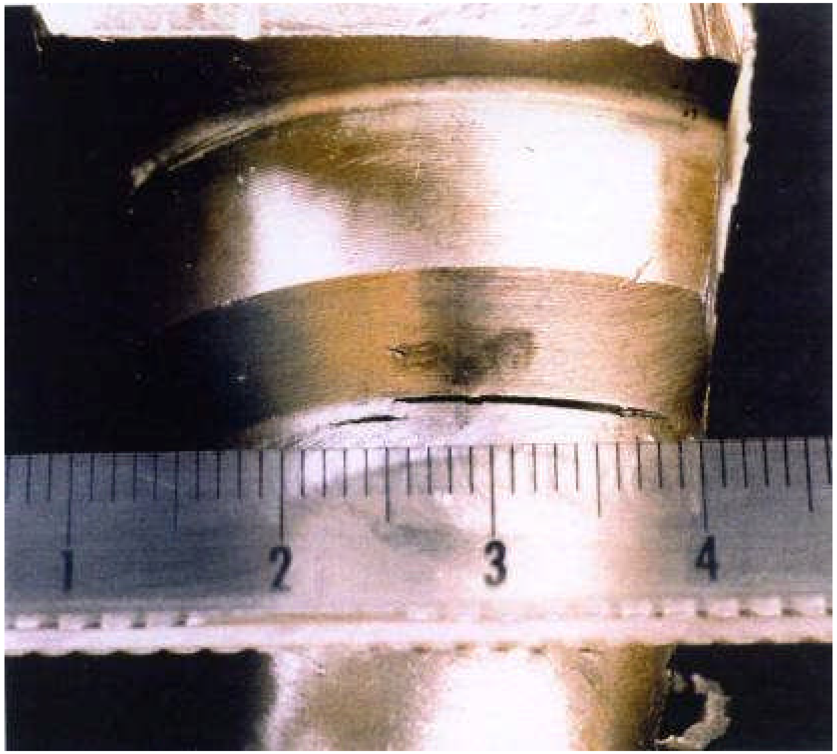
HYDROGEN CYLINDER BURSTS
INTERGRANULAR CRACK

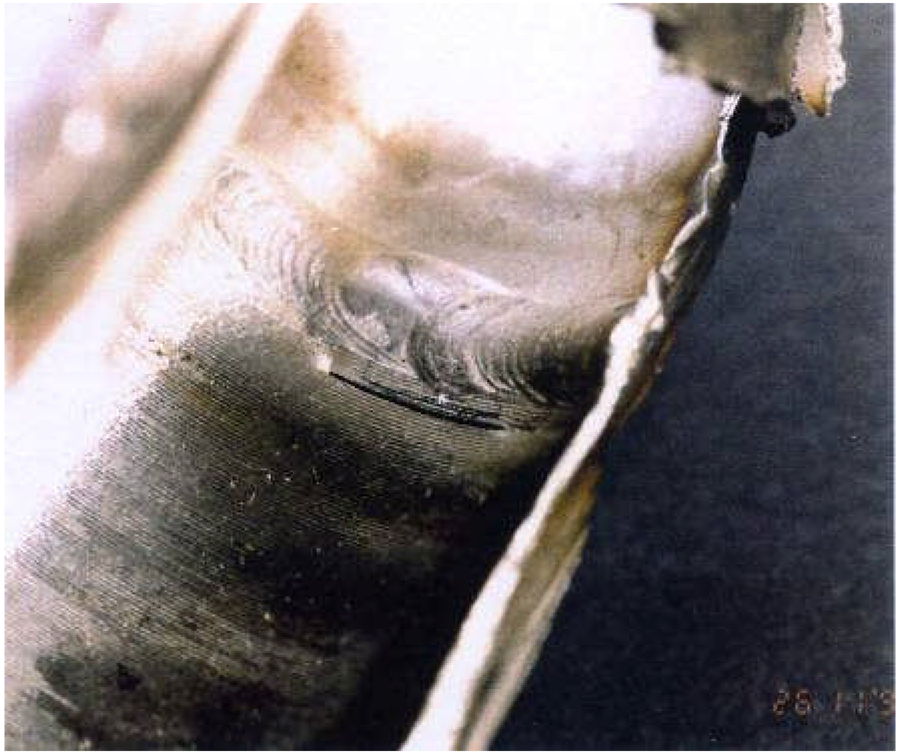
3. REPORTED ACCIDENTS AND INCIDENTS ON HYDROGEN EMBRITTLEMENT

VIOLENT RUPTURE
OF A HYDROGEN STORAGE VESSEL

3. REPORTED ACCIDENTS AND INCIDENTS ON HYDROGEN EMBRITTLEMENT

AIR LIQUIDE





H2 VESSEL. HYDROGEN CRACK ON STAINLESS STEEL PIPING

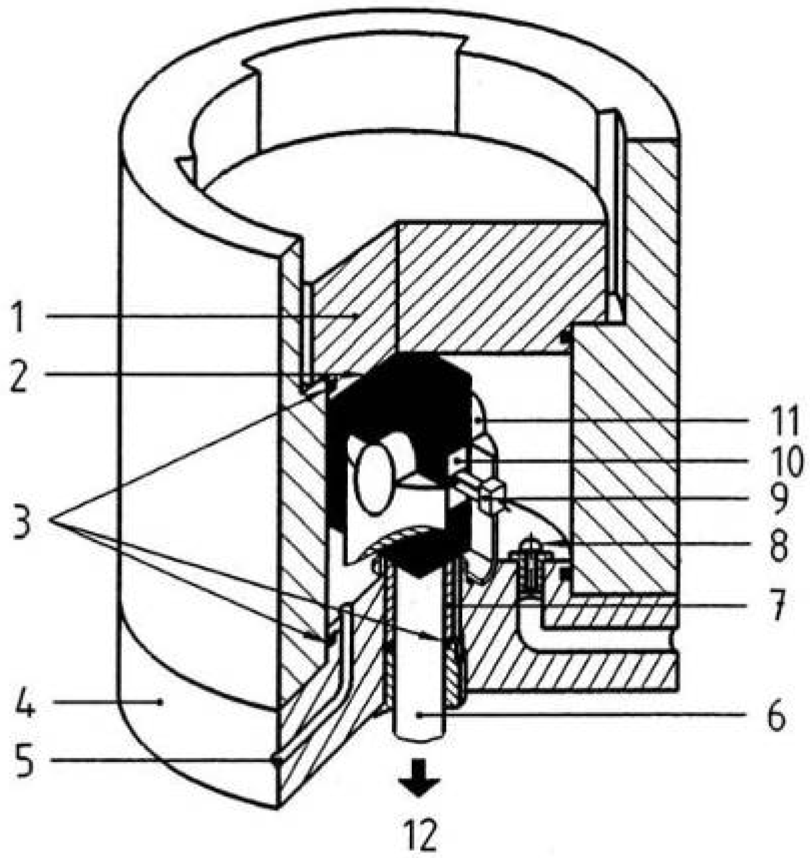
4. TEST METHODS

- Static (delayed rupture test)
- Dynamic → Constant strain rate
- Dynamic → Fatigue

4. TEST METHODS

- Fracture mechanic (CT, WOL, …)
- Tensile test
- Disk test
- Other mechanical test (semi-finished products)
- Test methods to evaluate hydrogen permeation and trapping

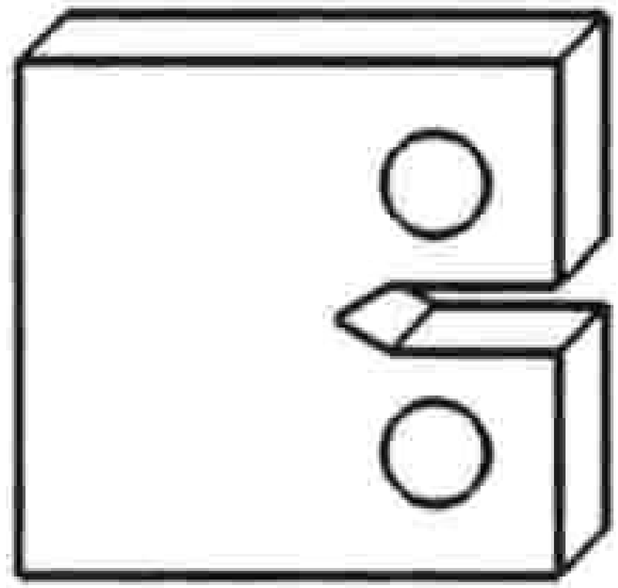
4. TEST METHODS



1. Vessel head
2. Specimen
3. O-rings
4. Vessel bottom
5. Gas inlet – Gas outlet
6. Torque shaft
7. Load cell
8. Instrumentation feed through
9. Crack opening displacement gauge
10. Knife
11. Axis
12. Load application

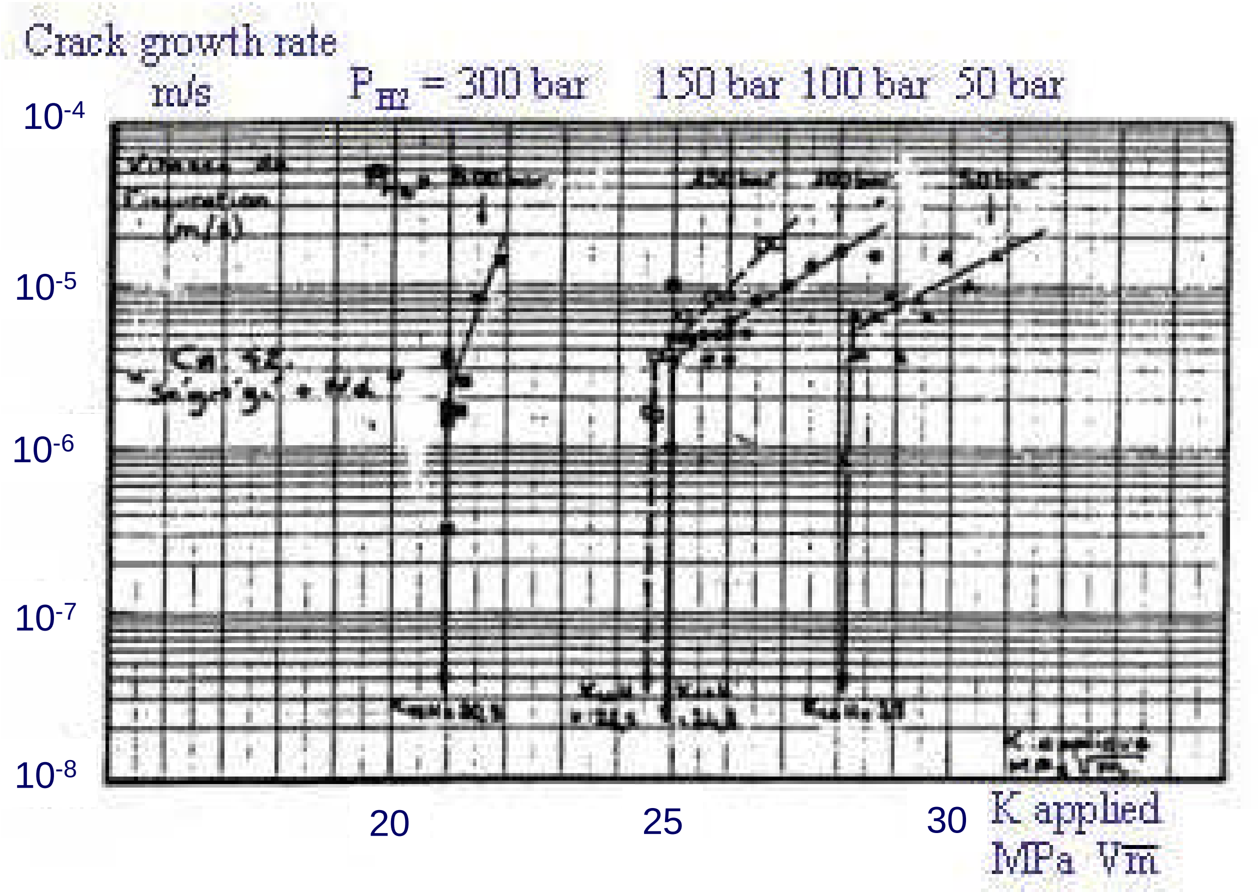
Fracture mechanics test with WOL type specimen

4. TEST METHODS



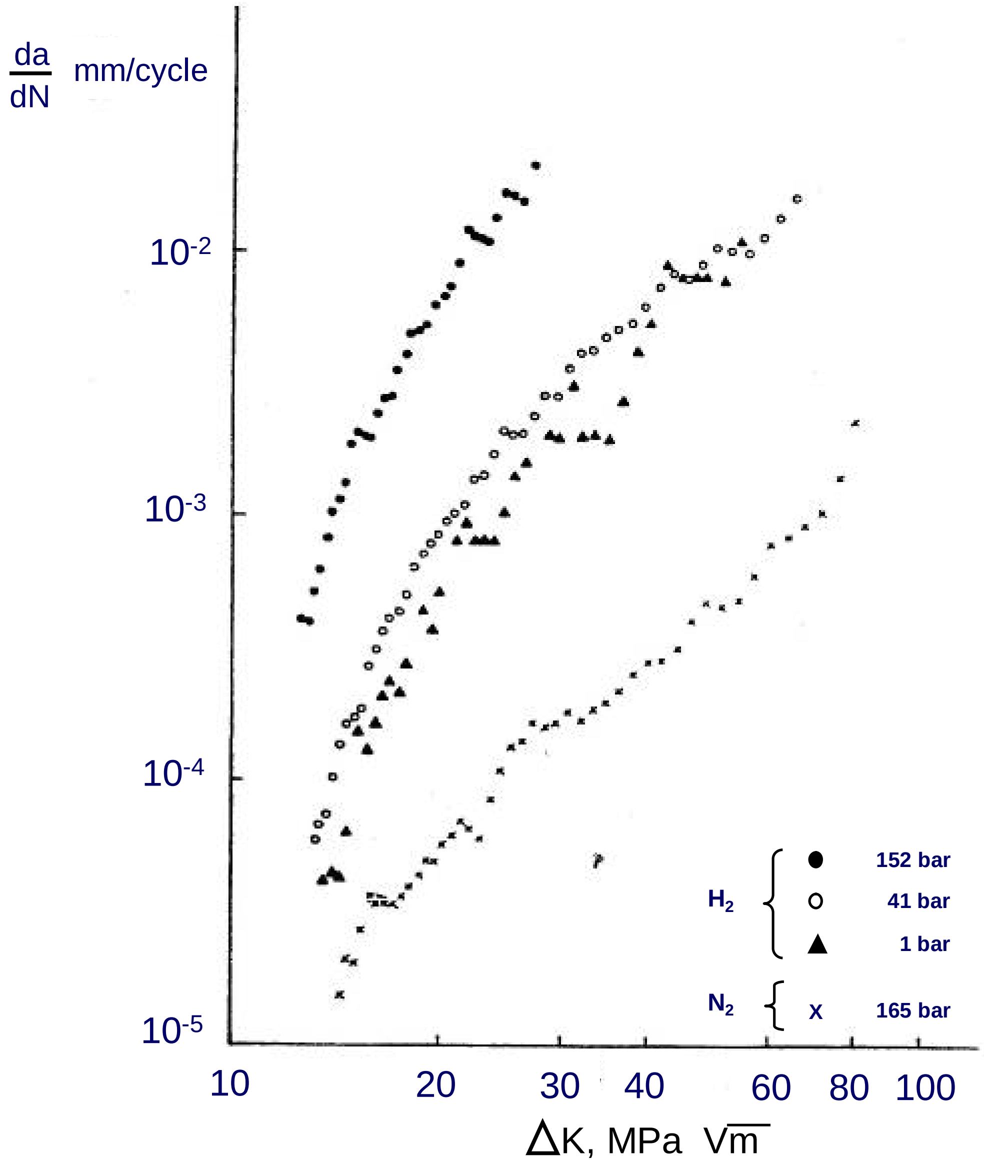
Specimens for compact tension test

4. TEST METHODS



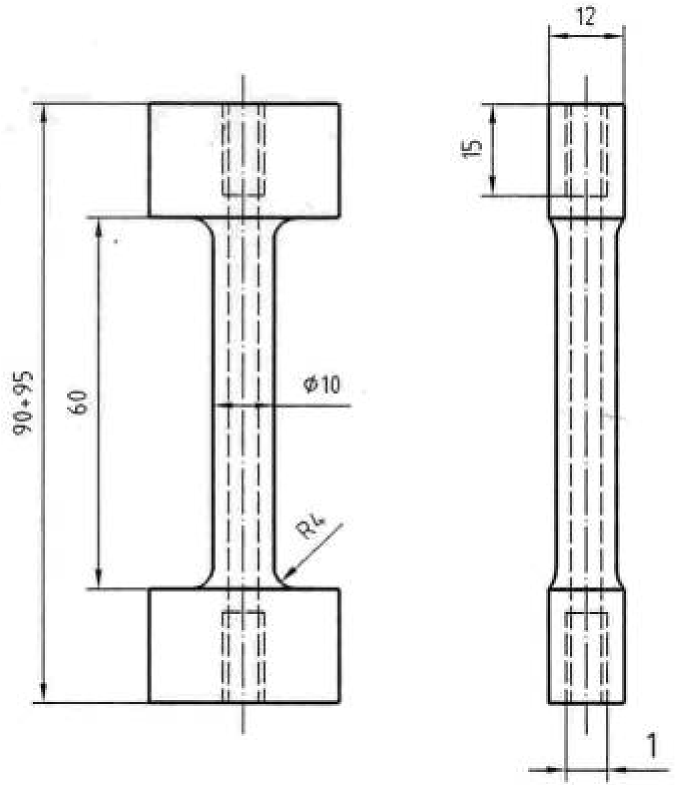
Influence of hydrogen pressure (300, 150, 100 and 50 bar) - Crack growth rate versus K curves

4. TEST METHODS



Influence of hydrogen pressure by British Steel

4. TEST METHODS



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

4. TEST METHODS

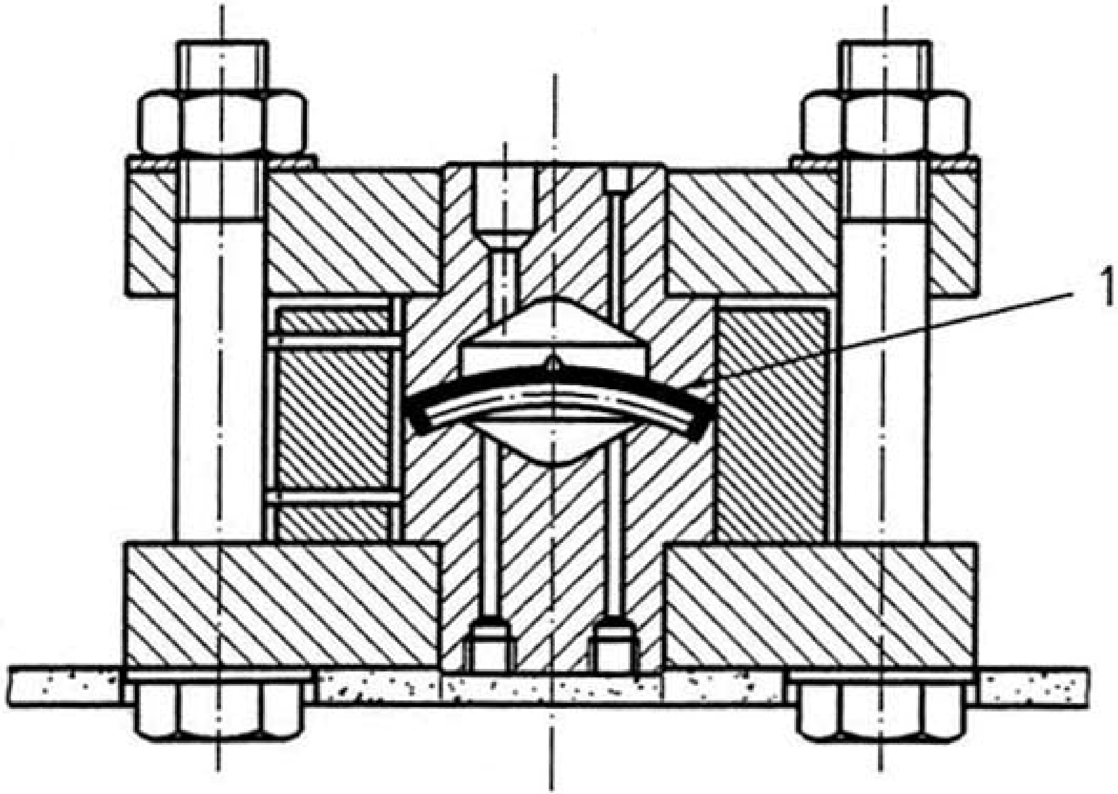
- $I = (\% RA_N - \% RA_H) / \% RA_N$

  I = Embrittlement index

  RA_N = Reduction of area without H_2

  RA_H = Reduction of area with H_2

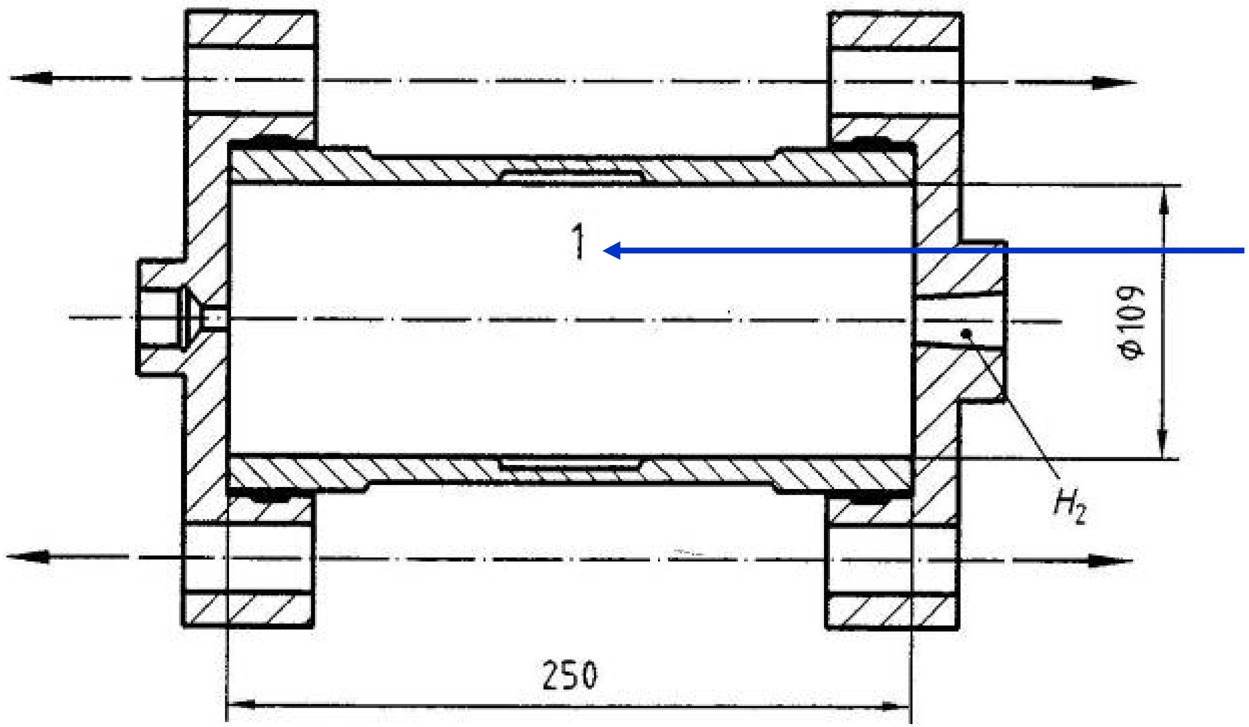
4. TEST METHODS



Pseudo Elliptic Specimen

Cell for delayed rupture test with Pseudo Elliptic Specimen

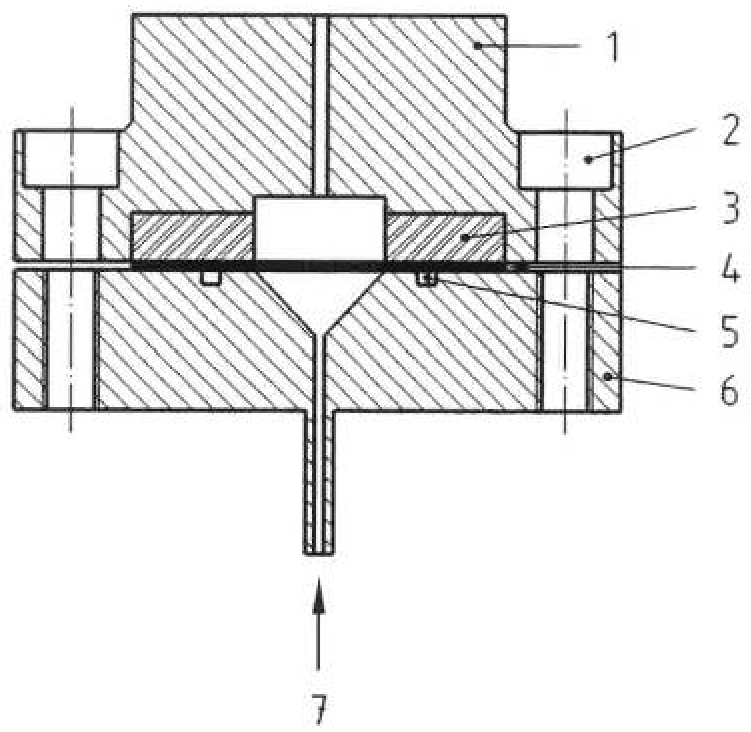
4. TEST METHODS



Inner notches with elongation measurement strip

Tubular specimen for hydrogen assisted fatigue tests

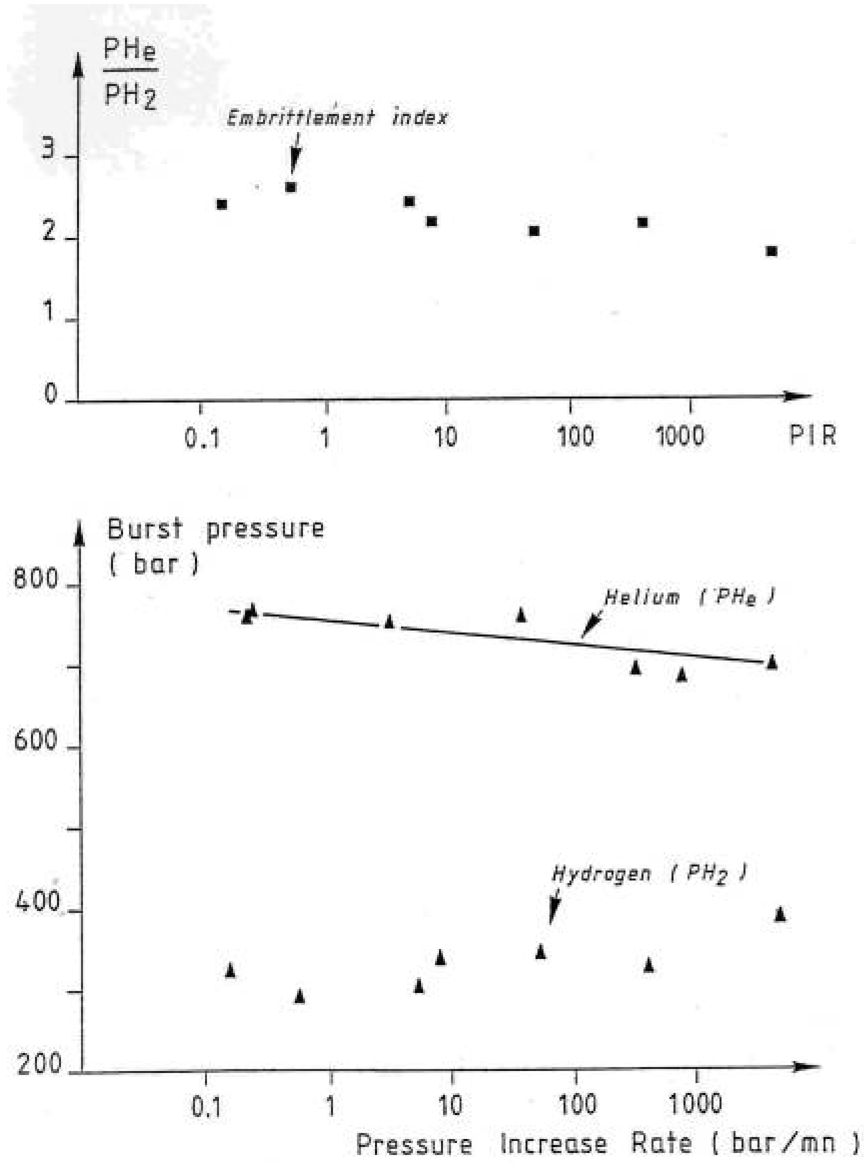
4. TEST METHODS



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

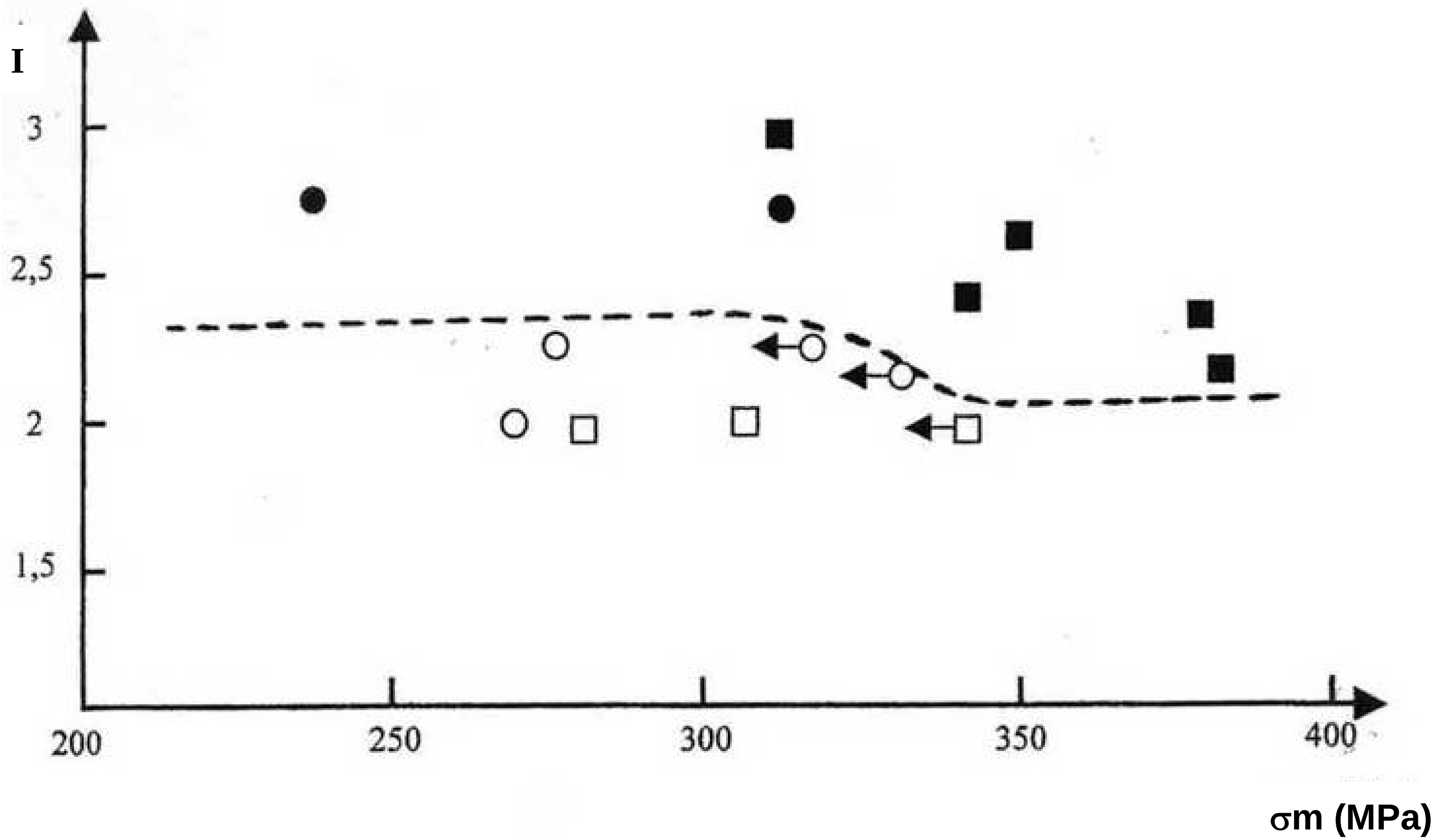
Disk testing method – Rupture cell for embedded disk-specimen

4. TEST METHODS



Example of a disk rupture test curve

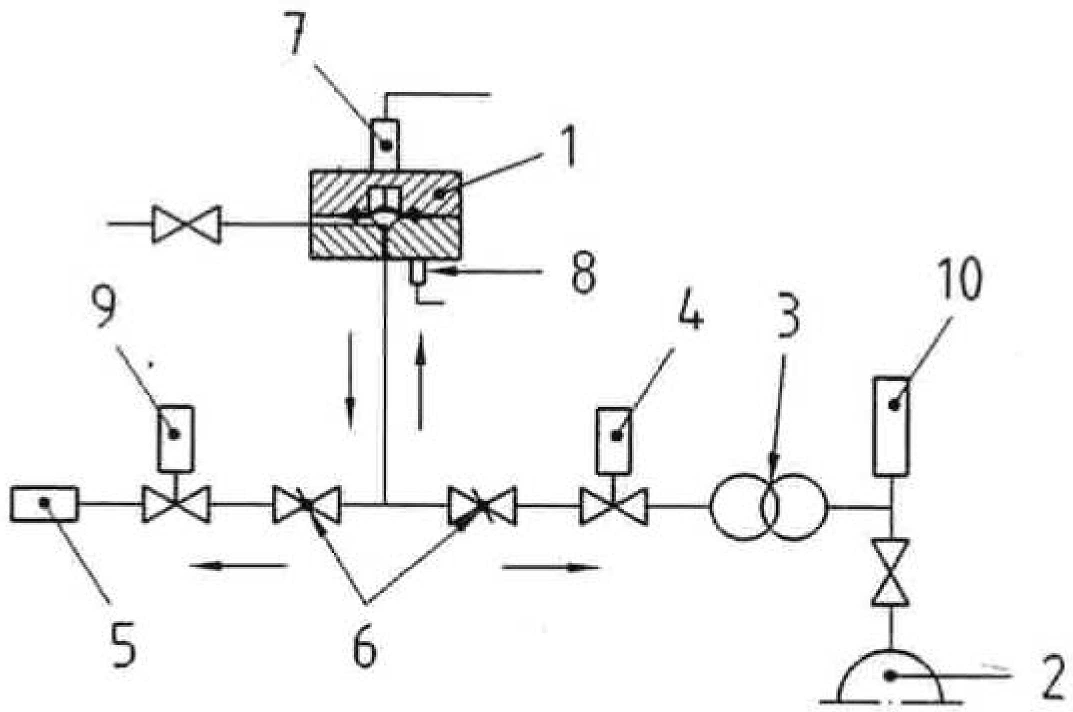
4. TEST METHODS



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

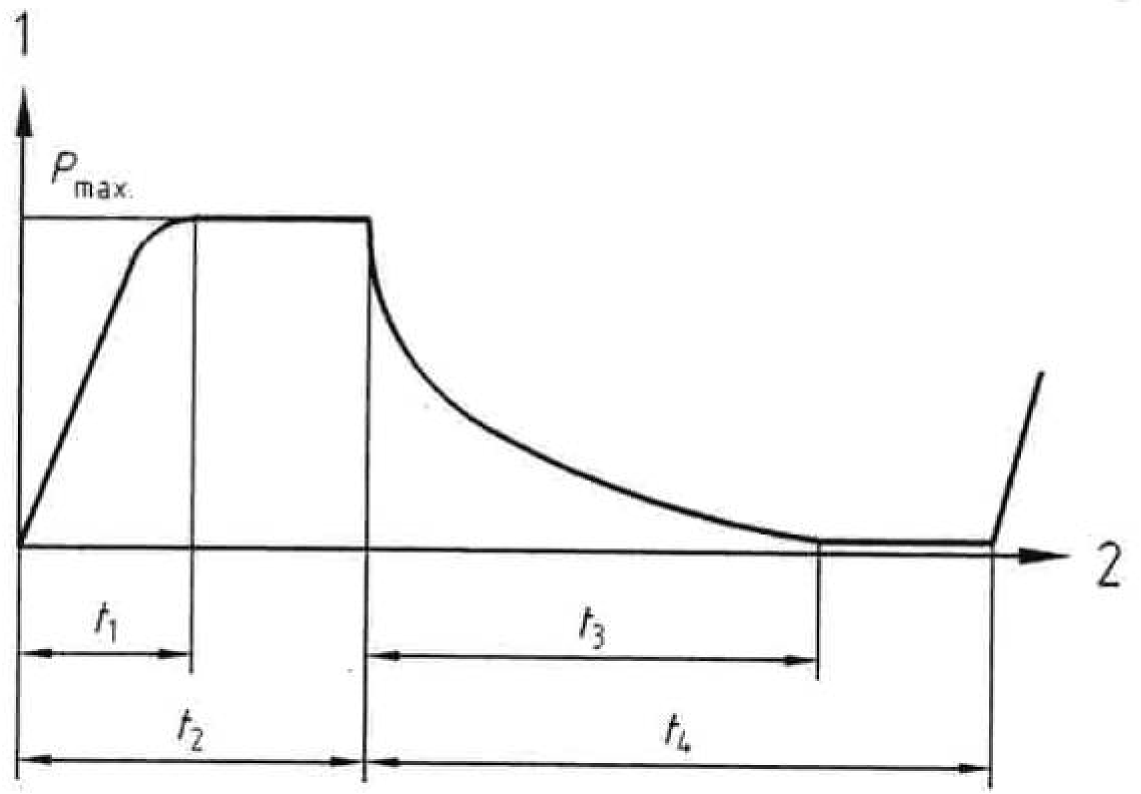
4. TEST METHODS

AIR LIQUIDE



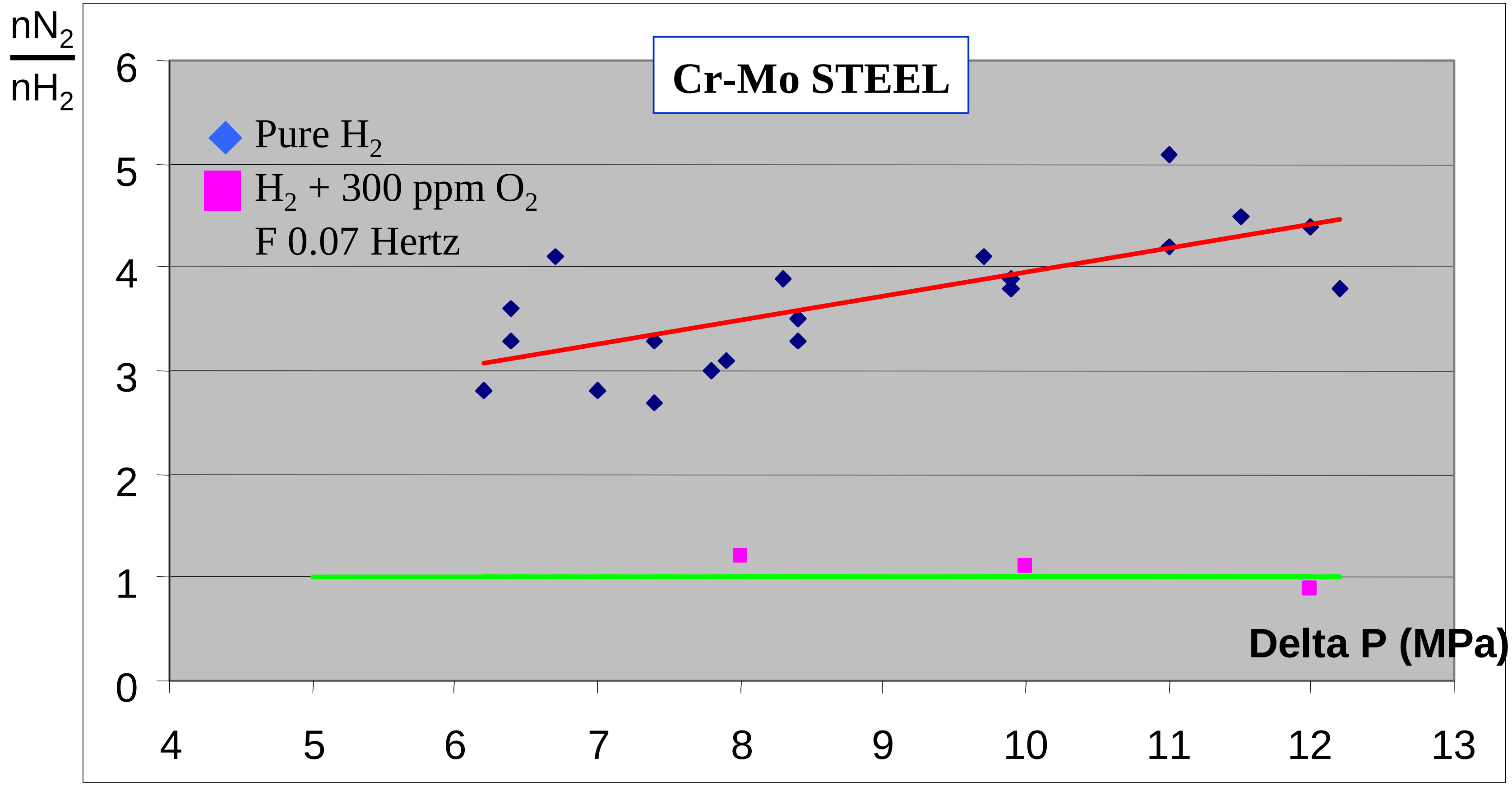
Fatigue test - Principle

4. TEST METHODS

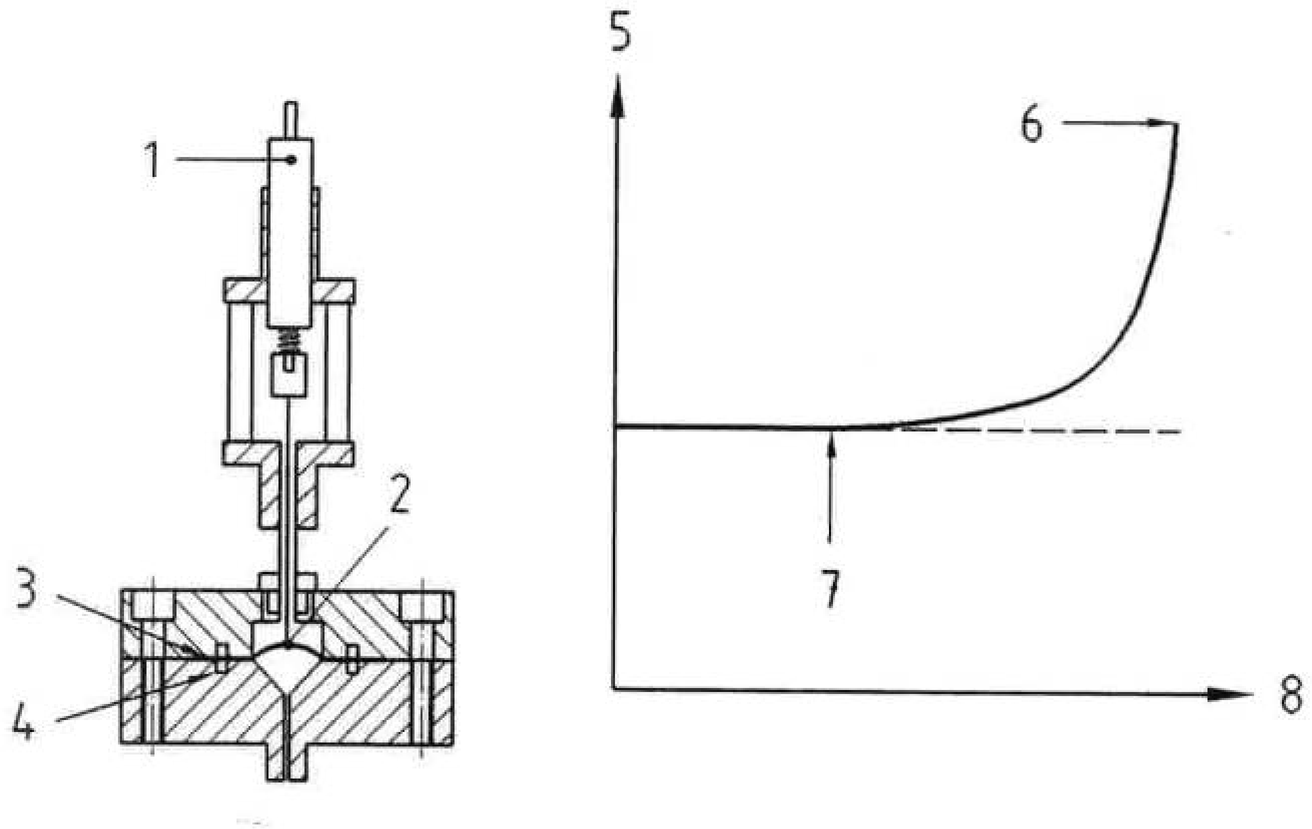


Fatigue test - Pressure cycle

AIR LIQUIDE



Fatigue tests, $\frac{nN_2}{nH_2}$ versus Δ P curves



Fatigue test

Principle to detect fatigue crack initiation

4. TESTS CHARACTERISTICS

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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 test	External	Dislocations
Cathodic charging test	External	Diffusion

4. 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 test	Small size and simple	Small size and very simple	Electrochemical equipment (potentiostat)

4. TESTS CHARACTERISTICS

AIR LIQUIDE

Interpretation of results

TESTS	TESTS SENSIBILITY	POSSIBILITY OF RANKING MATERIALS	SELECTION OF MATERIALS – EXISTING CRITERIA	PRACTICAL DATA TO PREDICT IN SERVICE PERFORMANCE
Disk rupture	High sensitivity	Possible	Yes $P_{H}e/P_{H2}$	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} - 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

5. PARAMETERS AFFECTING HYDROGEN EMBRITTLEMENT OF STEELS

5.1. Environment

5.2. Design and surface conditions

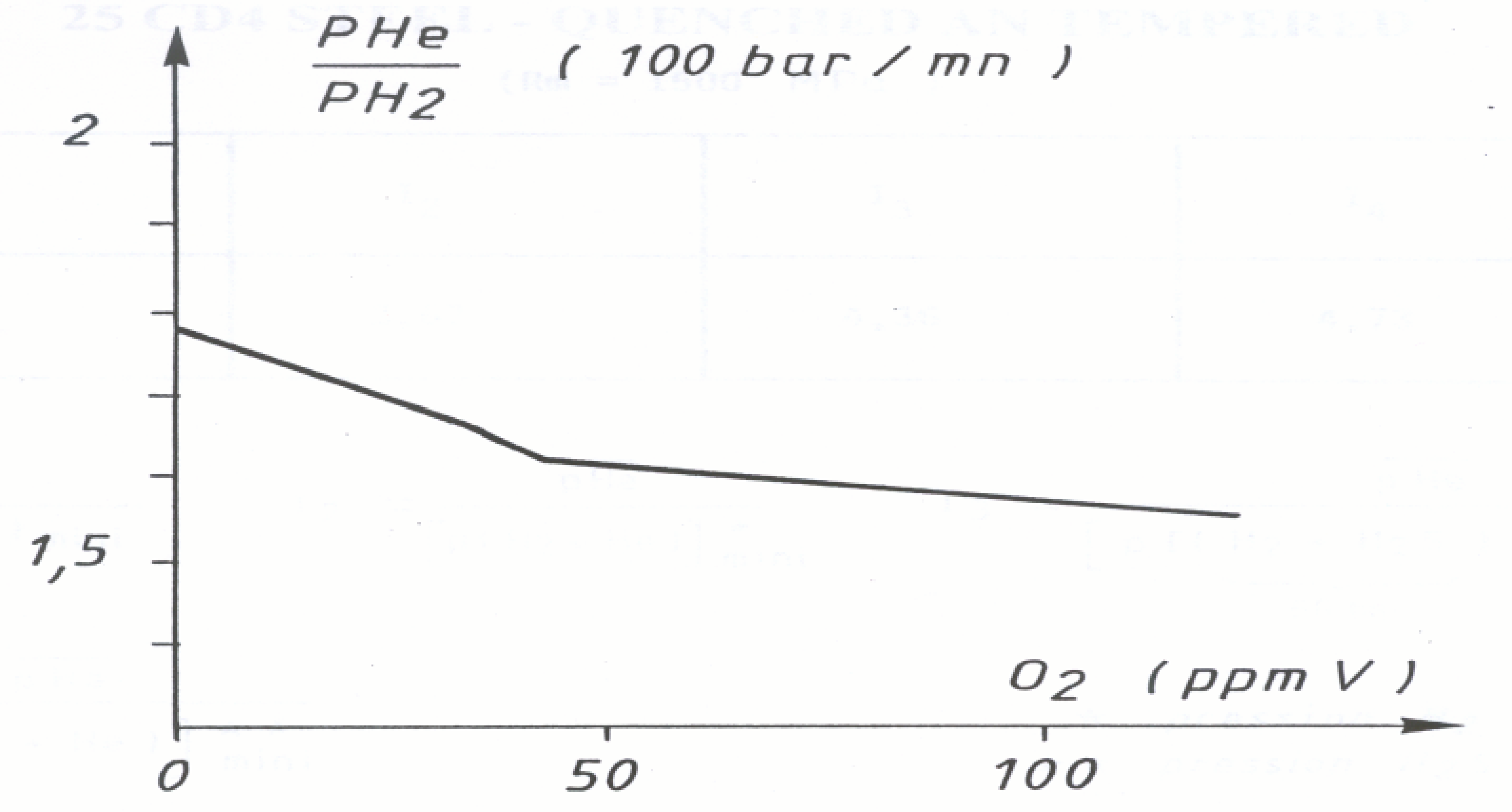
5.3. Material

5.1. Environment or "operating conditions"

- **Hydrogen purity**
- **Hydrogen pressure**
- **Temperature**
- **Stresses and strains**
- **Time of exposure**

5.1. Environment or "operating conditions"

- **Hydrogen purity**



Influence of oxygen contamination

5.1. Environment or "operating conditions"

Hydrogen purity

(Rm = 1500 MPa)

I_1	I_2	I_3	I_4
3,88	3,67	4,36	4,73

$$I_1 = \frac{\overline{p\ He}}{(p\ H_2\ pur)_{mini}}$$

$$I_2 = \frac{\overline{p\ He}}{[p\ (H_2 + He)]^{*}_{mini}}$$

$$I_3 = \frac{\overline{p\ He}}{[p\ [\underbrace{(H_2 + H_2S) + He}_{50\ bar}]]_{mini}}$$

$$I_4 = \frac{\overline{p\ He}}{[p\ (H_2S + He)]^{**}_{mini}}$$

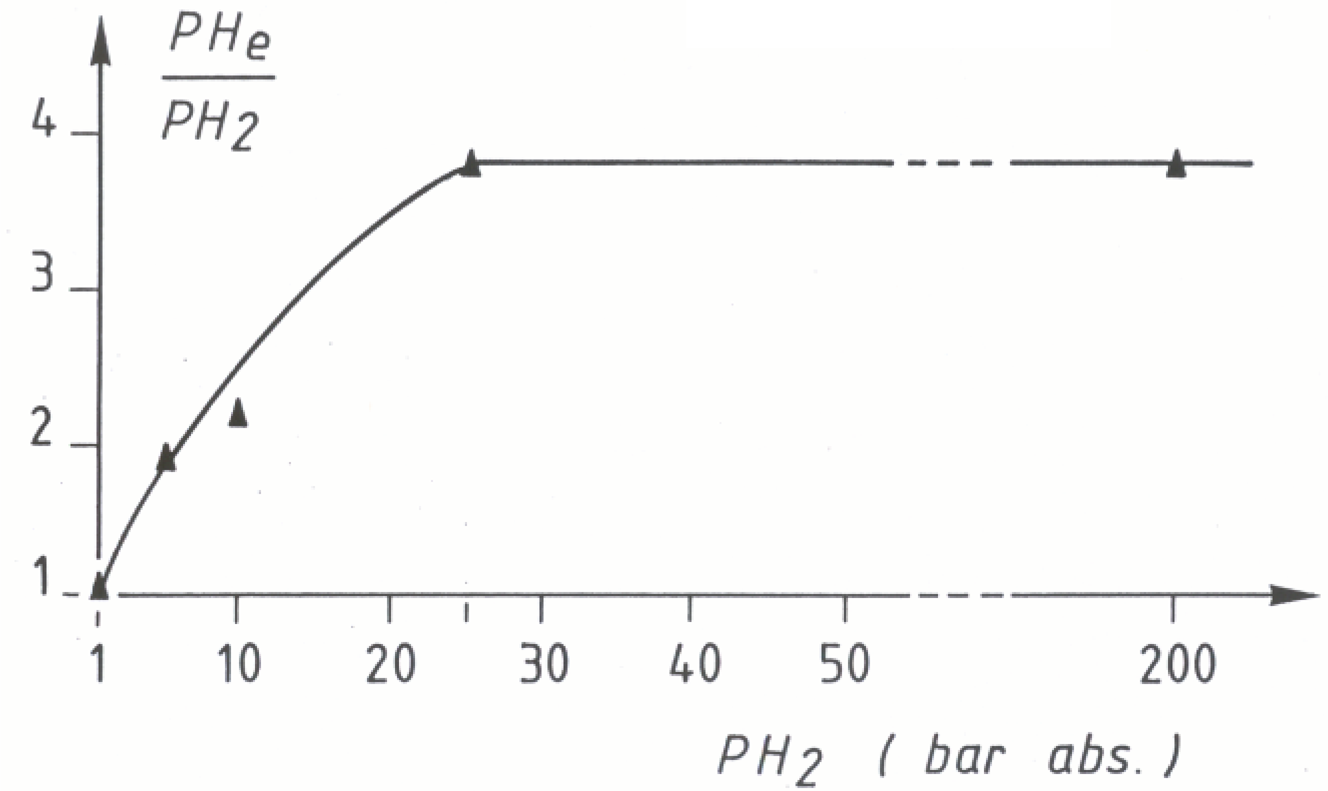
* H_2 pressure = 50 bar

** H_2S pressure = 18 bar

Influence of H_2S contamination

5.1. Environment or "operating conditions"

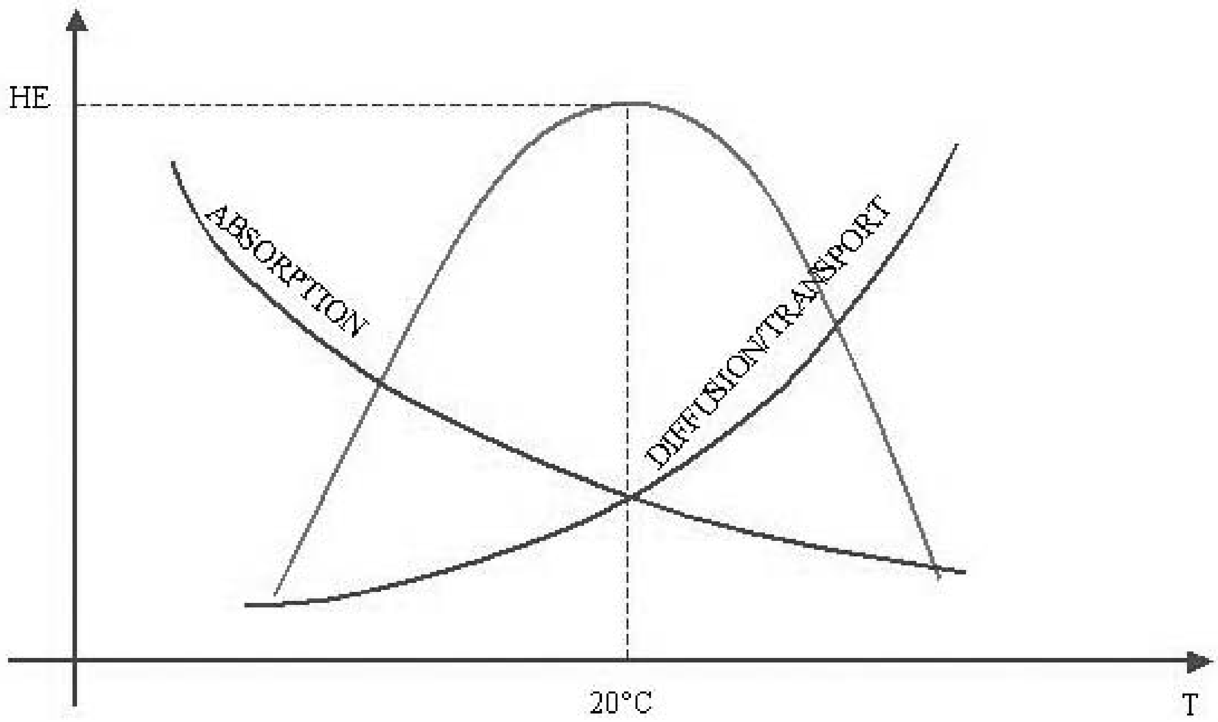
- **Hydrogen pressure**



Influence of H_2S partial pressure for AISI 321 steel

5.1. Environment or "operating conditions"

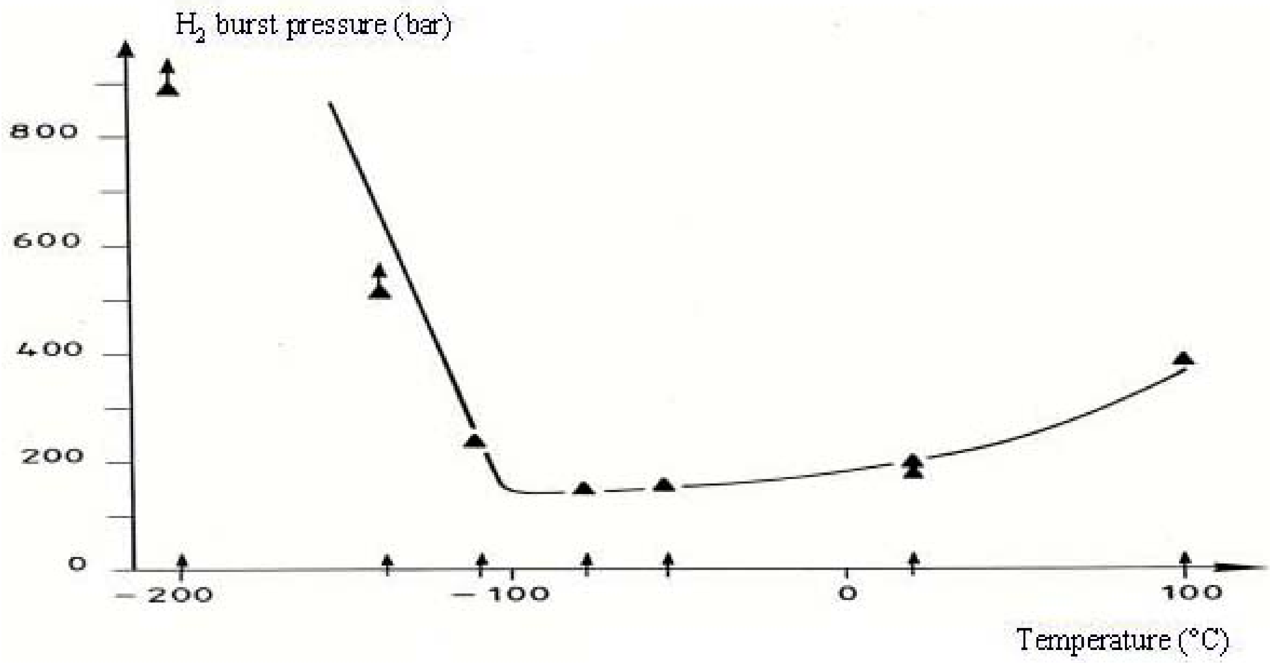
- **Temperature**



Influence of temperature - Principle

5.1. Environment or "operating conditions"

- **Temperature**



Influence of temperature for some stainless steels

5.1. Environment or “operating conditions”

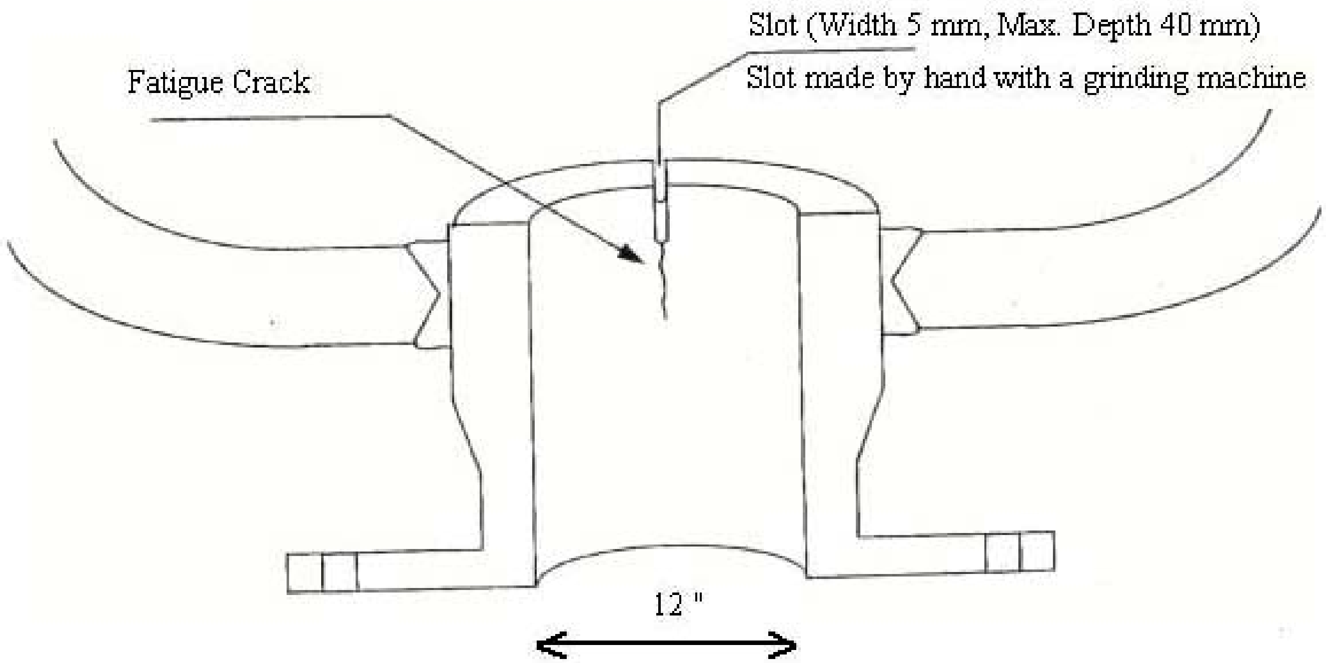
- Hydrogen purity
- Hydrogen pressure
- Temperature
- **Stresses and strains**
- **Time of exposure**

5.2. Design and surface conditions

- **Stress level**
- **Stress concentration**
- **Surface defects**

5.2. Design and surface conditions

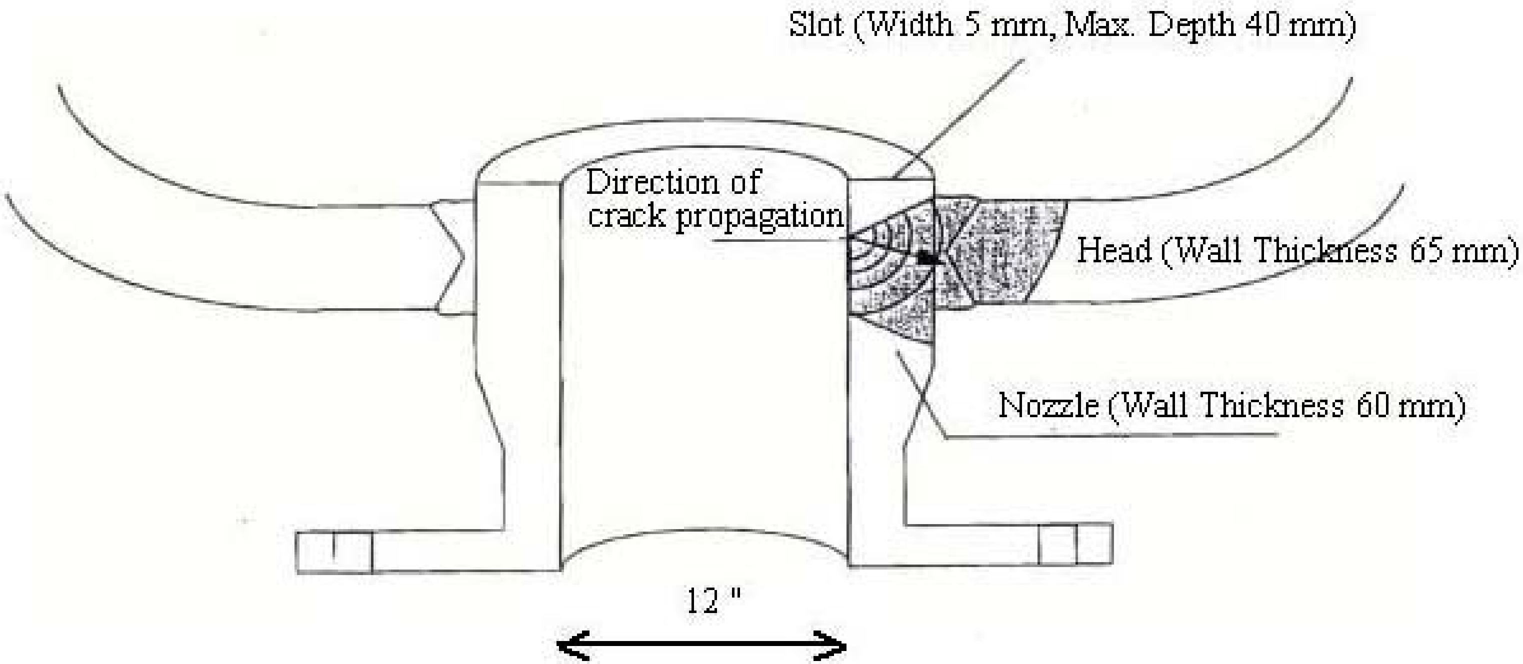
- **Stress concentration**



Crack initiation on a geometrical discontinuity

5.2. Design and surface conditions

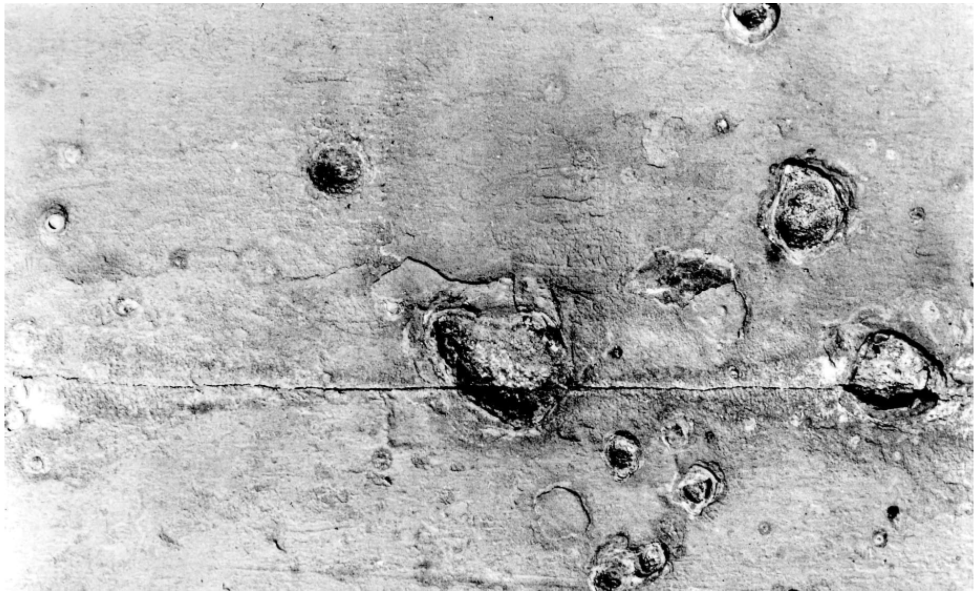
Stress concentration



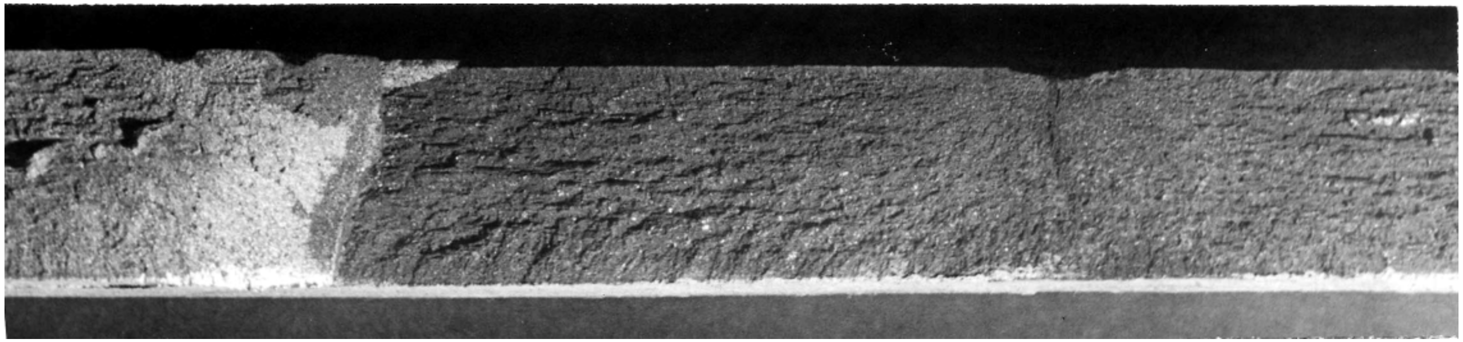
Crack initiation on a geometrical discontinuity

5.2. Design and surface conditions

Surface defects



FAILURE OF A HYDROGEN TRANSPORT VESSEL IN 1983. HYDROGEN CRACK INITIATED ON INTERNAL CORROSION PITS



5.3. Material

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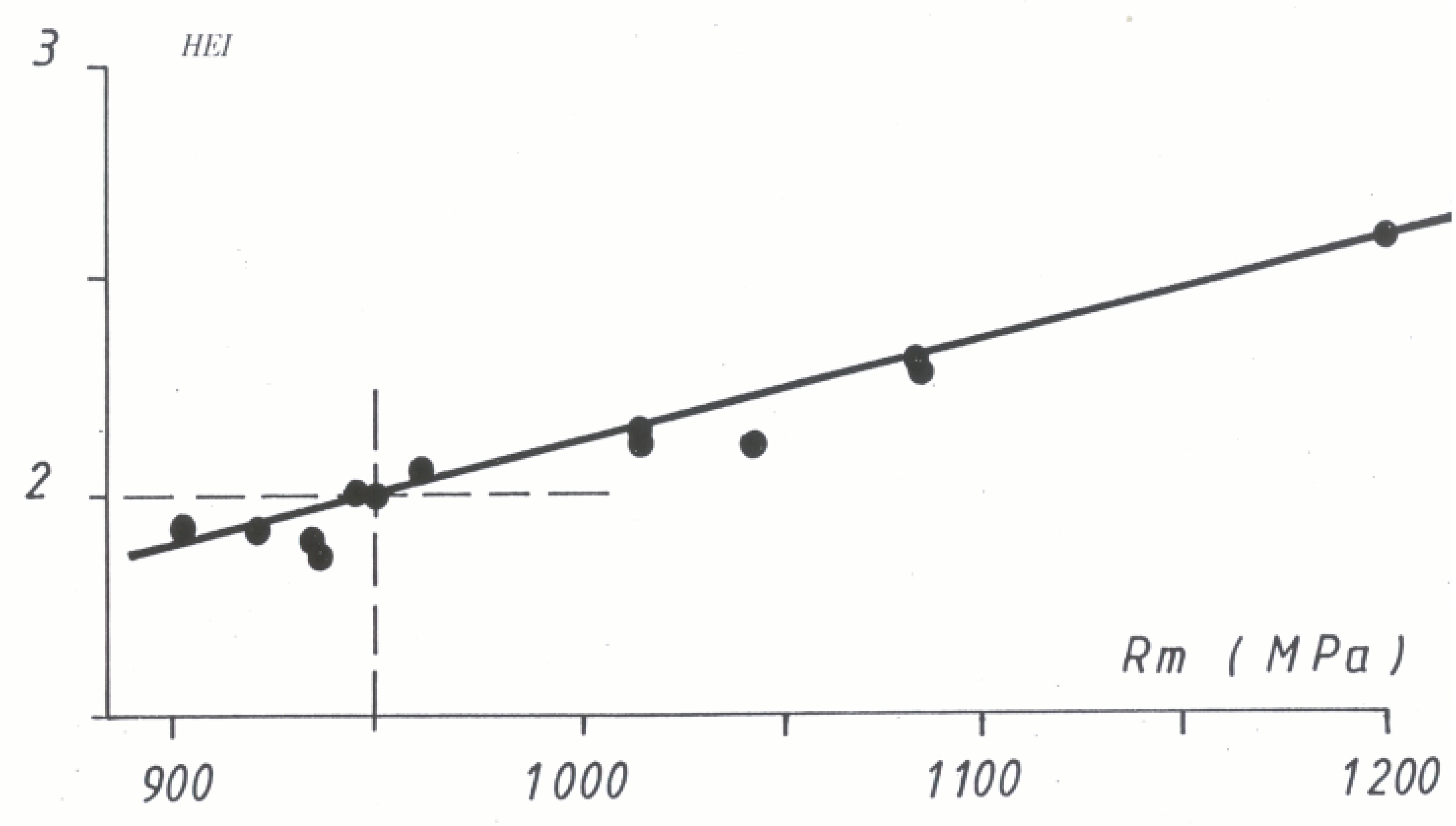
- Microstructure
- Chemical composition
- Heat treatment and mechanical properties
- Welding
- Cold working
- Inclusion

5.3. Material

- **Heat treatment and mechanical properties**



5.3. Material

Welding

Ferrite content	0 % (No weld)	2.5 %	8 %	25 %
Embrittlement index	1.9	1.9	2.0	4.2

5.3. Material

- Microstructure
- Chemical composition
- Heat treatment and mechanical properties
- Welding
- **Cold working**
- **Inclusion**

6. HYDROGEN EMBRITTLEMENT OF OTHER MATERIALS

1) **All metallic materials present a certain degree of sensitive to HE**

2) **Materials which can be used**

- **Brass and copper alloys**
- **Aluminium and aluminium alloys**
- **Cu-Be**

6. HYDROGEN EMBRITTLEMENT OF OTHER MATERIALS

3) **Materials known to be very sensitive to HE :**

- **Ni and high Ni alloys**
- **Ti and Ti alloys**

4) **Steels : HE sensitivity depend on exact chemical composition, heat or mechanical treatment, microstructure, impurities and strength**

Non compatible material can be used at limited stress level

7. HYDROGEN ATTACK

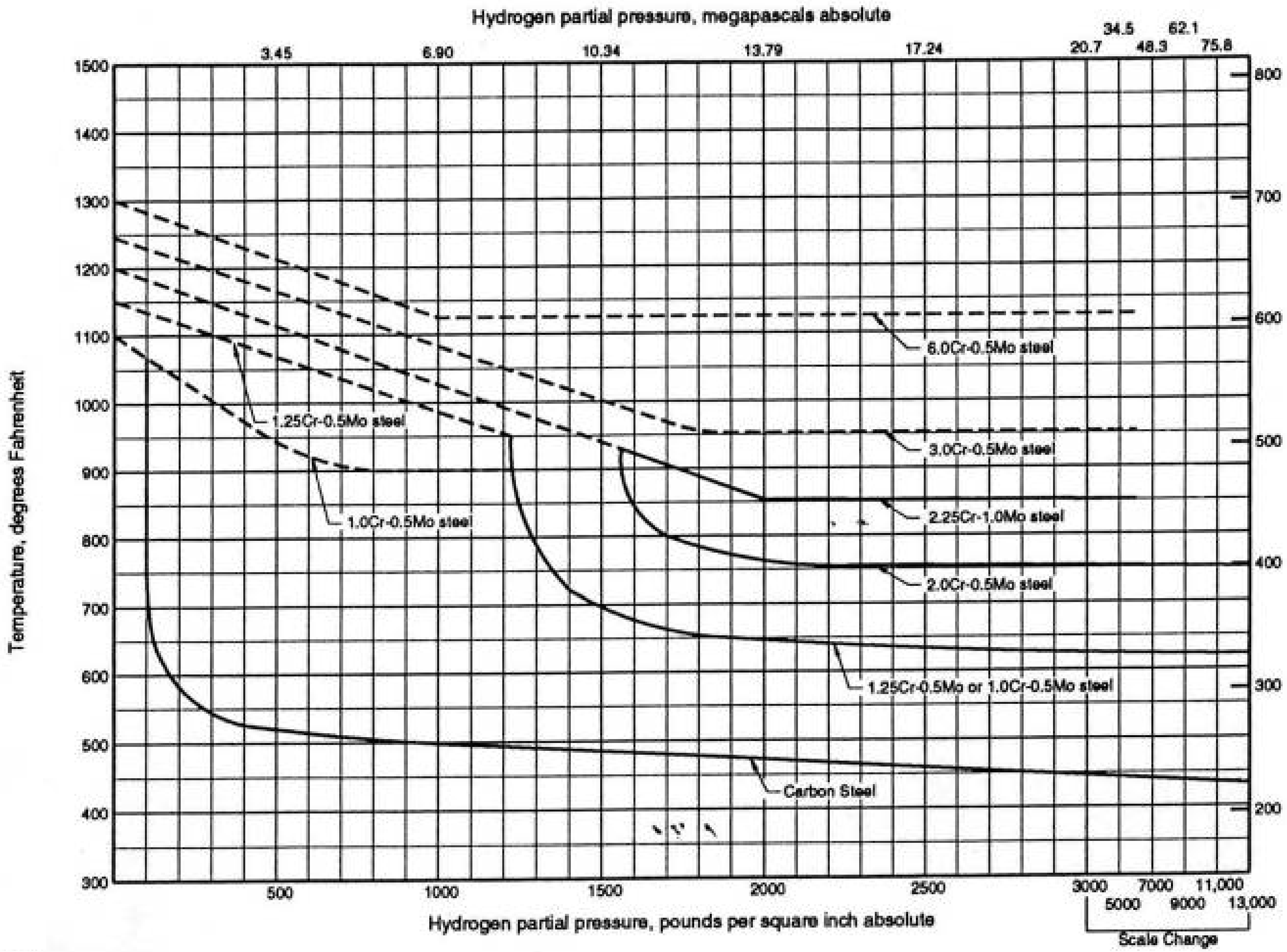
Main parameters summarized on the « Nelson curves » :

- **Influence of P, T, Cr and Mo**
- **Ti and W have also a beneficial effect**
- **C, Al, Ni and Mn (excess) have a detrimental effect**

Other parameters :

- **Heat treatment**
- **Stress level, welding procedure**

7. HYDROGEN ATTACK



Legend :

Surface decarburization - - - - - -

Internal decarburization ———

(Hydrogen attack)

Nelson curves

8. CONCLUSION - RECOMMENDATION

1) The influence of the different parameters shall be addressed.

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- **The material, i.e. the mechanical properties, chemical composition and heat treatment**

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- The material, i.e. the mechanical properties, chemical composition and heat treatment
- **The stress level of the equipment**

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- The material, i.e. the mechanical properties, chemical composition and heat treatment
- The stress level of the equipment
- **The surface defects and quality of finishing**

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- The « scope », i.e. the hydrogen pressure, the temperature and the hydrogen purity
- The material, i.e. the mechanical properties, chemical composition and heat treatment
- The stress level of the equipment
- The surface defects and quality of finishing
- **And the welding procedure, if any**