# Hydrogen embrittlement of steels.

H2FC
EUROPEAN INFRASTRUCTURE

San Sebastián Workshop
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- Hydrogen damage
- Hydrogen damage and steel
- Hydrogen loading
- How to study hydrogen embrittlement
- Assessment of the hydrogen embrittlement sensitivity

# Hydrogen damages

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Hydrogen

Interaction

Metallic alloys

Degradation process due to hydrogen load

**Hydrogen damage**

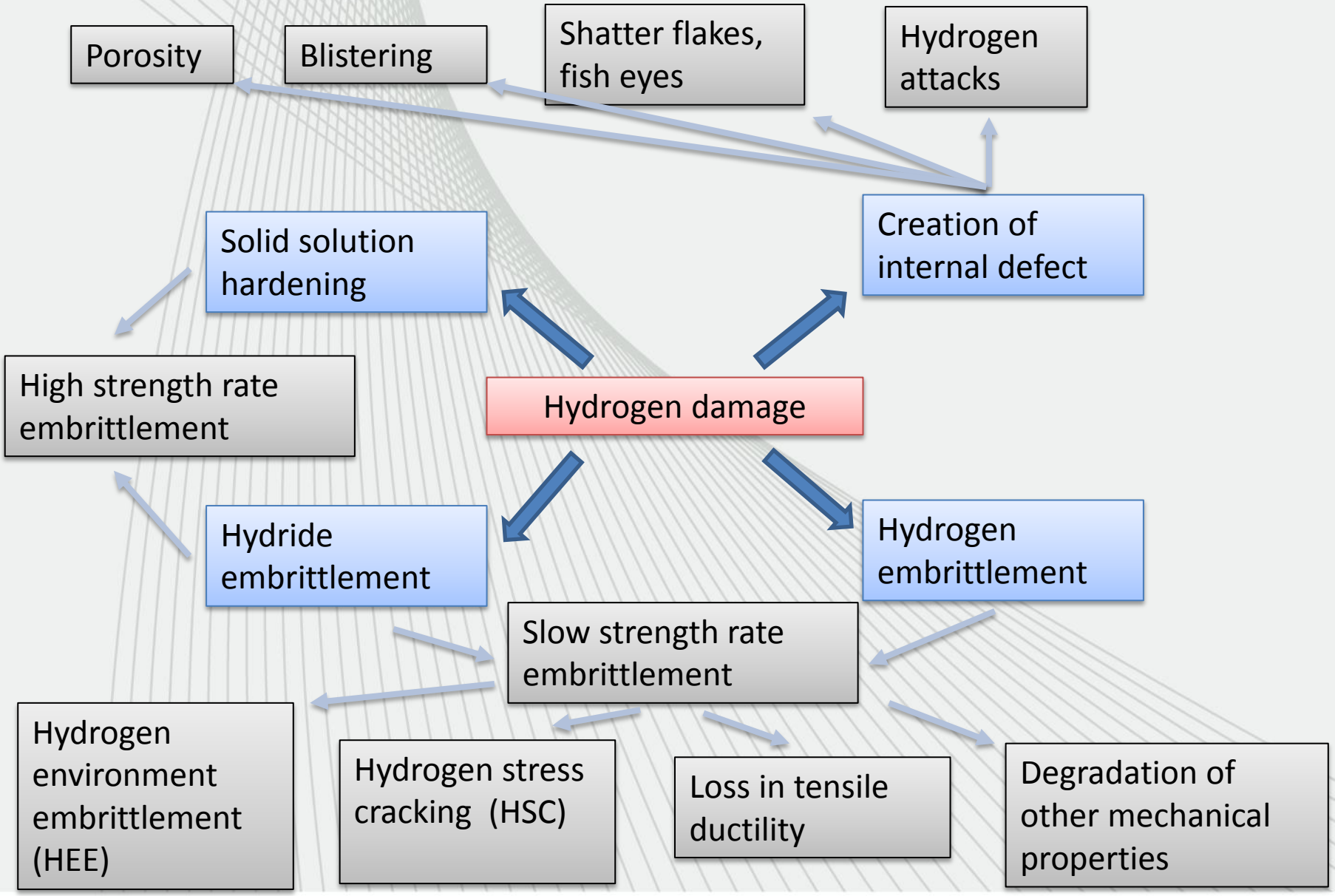
# Hydrogen damage

# Historical problem

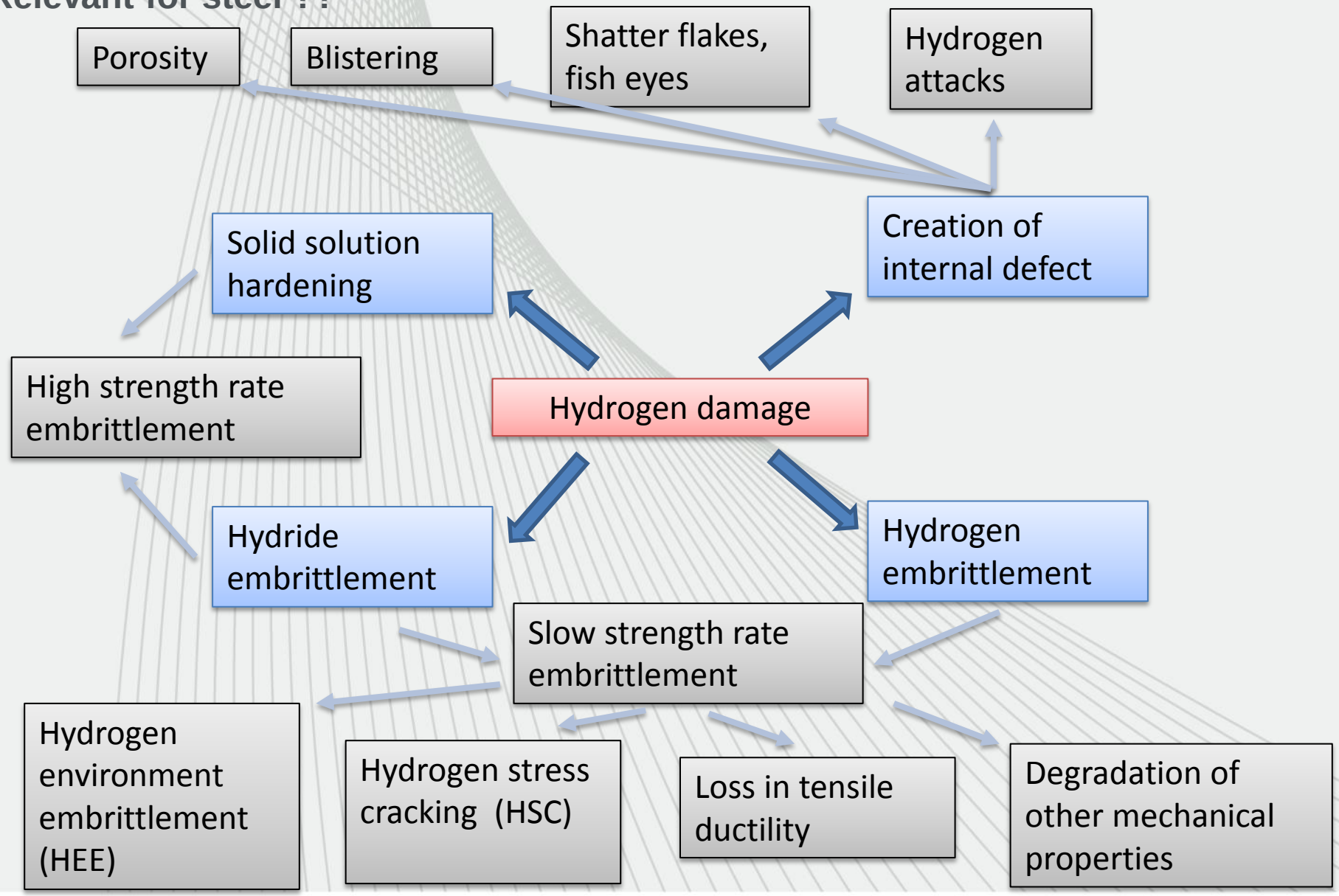
Observed since the beginning of modern metallurgy (end of XIX$^{th}$ century)

e.g. : in 1875 W. H. Johnson reported: “some remarkable changes produced in iron by the action of hydrogen and acids”.*

* W. H. Johnson, Proc. Royal Soc. (London), 23 (1875), 168


Porosity
Blistering
Shatter flakes, fish eyes
Hydrogen attacks
Solid solution hardening
Creation of internal defect
High strength rate embrittlement
Hydrogen damage
Hydride embrittlement
Hydrogen embrittlement
Slow strength rate embrittlement
Hydrogen environment embrittlement (HEE)
Hydrogen stress cracking (HSC)
Loss in tensile ductility
Degradation of other mechanical properties

## Relevant for steel ??



## Relevant for steel ??

~~Solid solution hardening~~

~~High strength rate embrittlement~~

Hydrogen damage

Mainly
Niobium and
Tantalum

Dissolution of hydrogen and embrittlement before the limit of solubility.
Embrittlement increase with the straining rate

## Relevant for steel ??

hydride forming with metals like titanium, zirconium and vanadium

High strength rate embrittlement

Hydrogen damage

Hydride embrittlement

Slow strength rate embrittlement

Hydrogen environment embrittlement (HEE)

Hydrogen stress cracking (HSC)

Loss in tensile ductility

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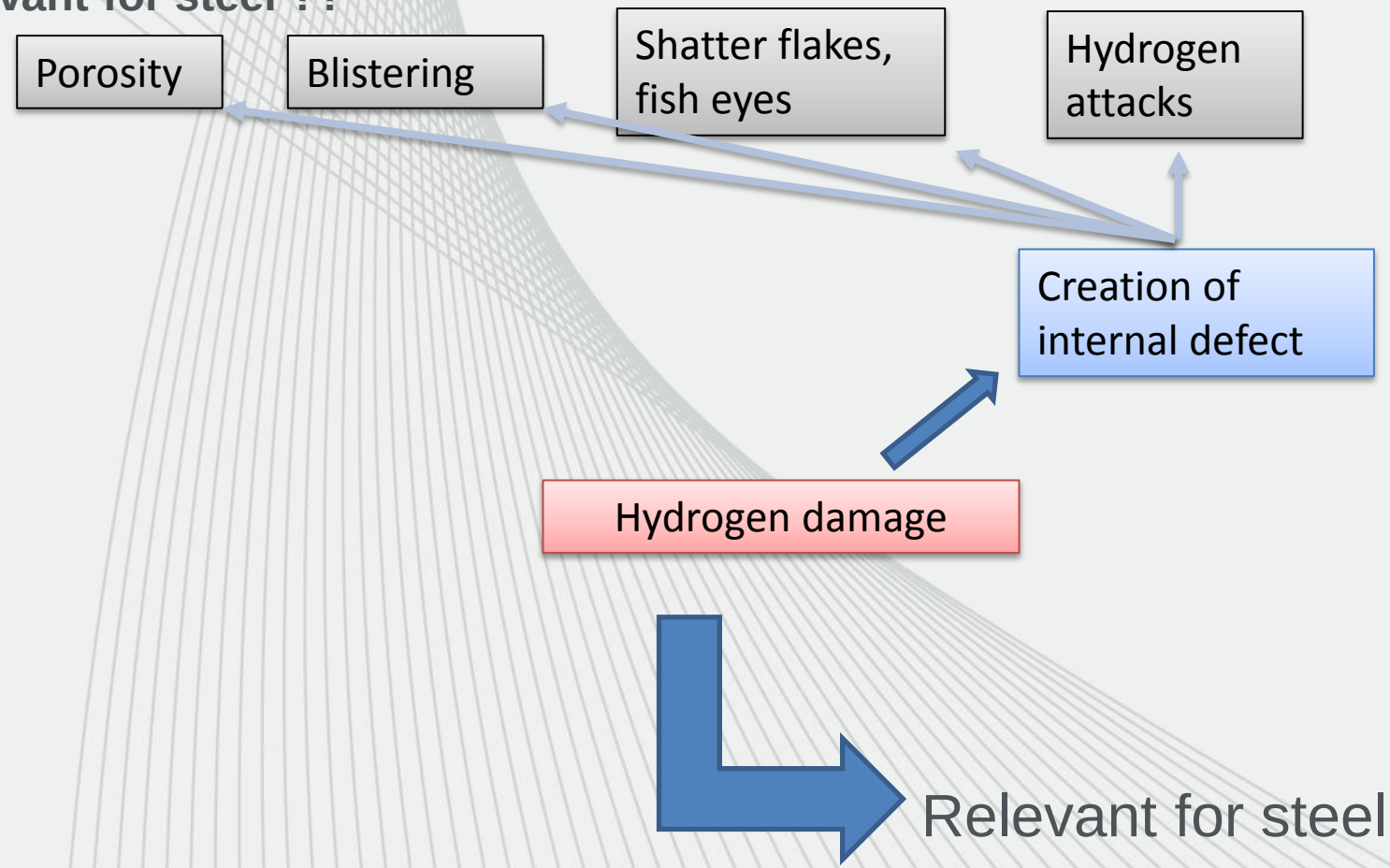
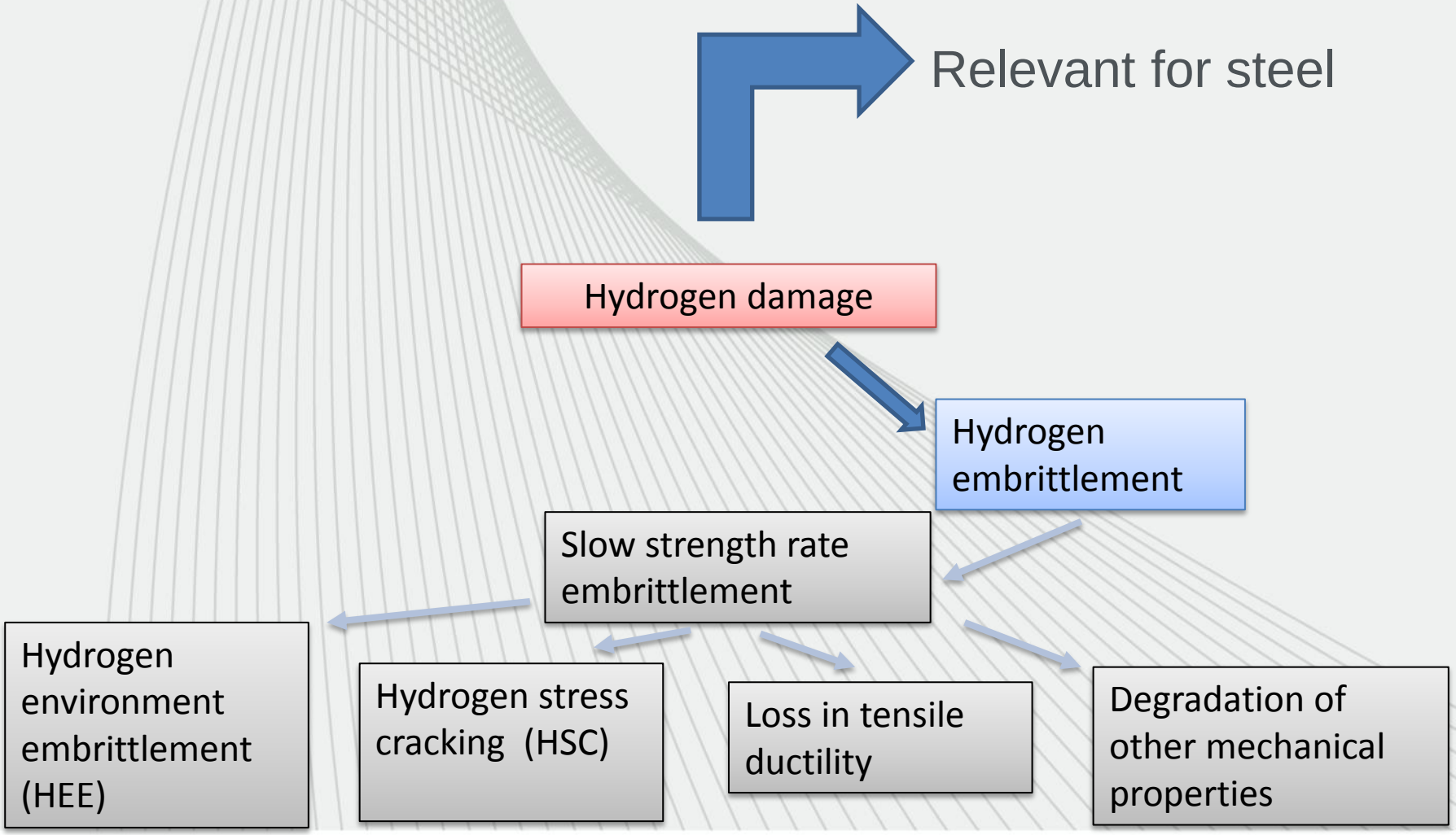
## Relevant for steel ??



# Relevant for steel ??



# Hydrogen damage and steel

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# Steel

# Main “nature of steels”

At least Iron and carbon (<2%, otherwise it is cast iron)

- carbon steel (Fe and C)
- Low alloyed steel : Fe, C plus other alloying elements, up to 10%, to give extra properties
- Stainless steel: Fe, C (<0.2%), Cr (>10.5%):
    - Austenitic : high content in Ni
    - Ferritic low content in Ni
    - Matensitic
    - Duplex : presence of both phase Ferritic and austenitic
        - Super duplex
        - hyperduplex

# High temperature degradation mechanism

# Hydrogen attack

- Carbon or low alloyed steel
- High temperature
- High pressure of hydrogen

Diffusion of hydrogen in the steel

Reaction between $H_2$ and C to form $CH_4$

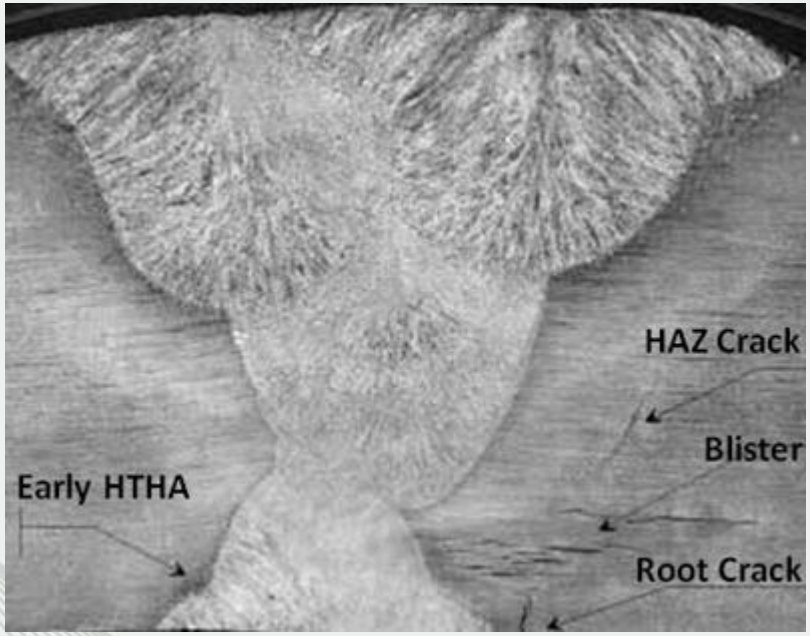
Close to the surface:

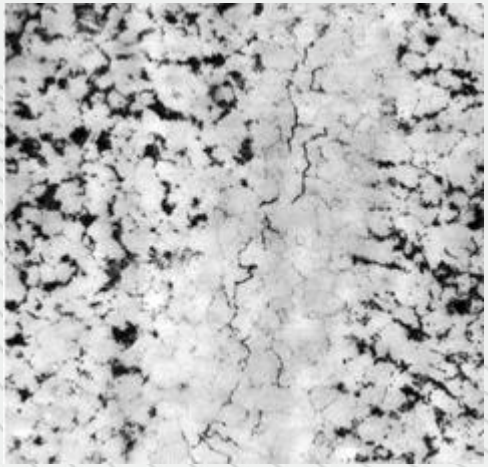
- release of $CH_4$

Delay

In the bulk:

- De-carburation of carbide (perlite): loss of mechanical properties
- Accumulation of methane in micro pores: initiation of cracks



# Low temperature degradation mechanism

# HIC, SOHIC, SWC: the “internal hydrogen” (bulk process)

- HIC: hydrogen induced cracking
- SOHIC: stress oriented hydrogen induced cracking
- SWC: stepwise cracking

Also referred as porosity, blistering, hydrogen induced blistering…

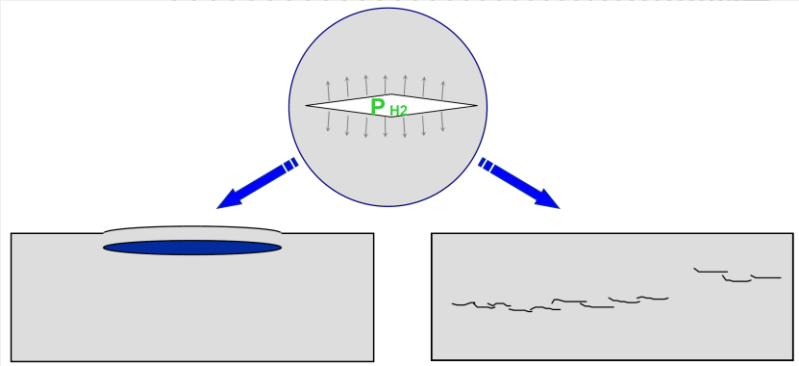
Requirement:

- Presence of porosity or micro voids
- Presence of hydrogen load
- The material remain ductile beside the presence of hydrogen

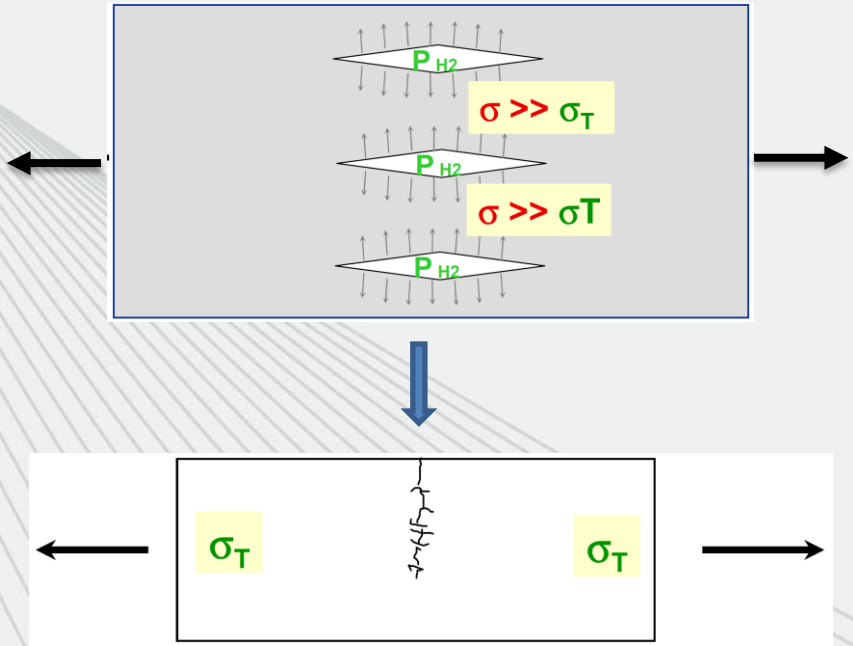
Ferritic steel particularly sensitive (e.g.: 8Cr-2Mo, 26Cr-1Mo, 29Cr-4Mo, 29Cr-4Mo-2Ni…)

# HIC, SOHIC, SWC: the “internal hydrogen”

HIC, SWC

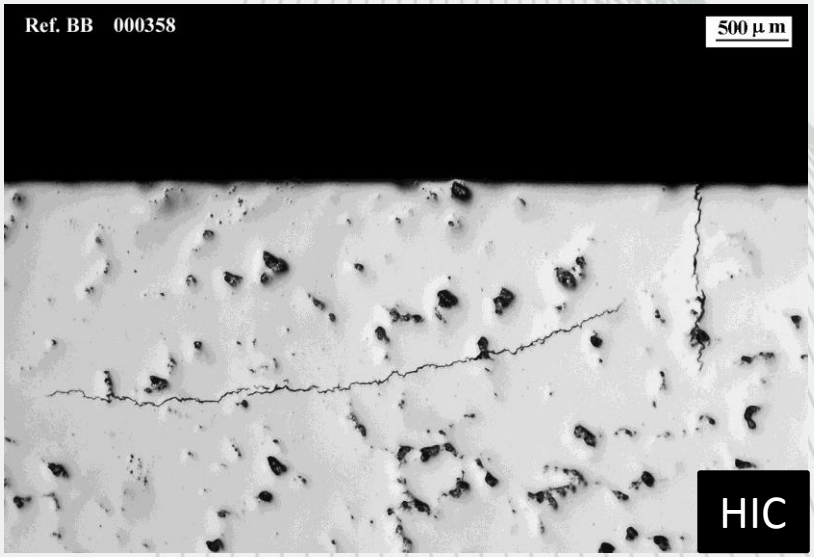



SOHIC

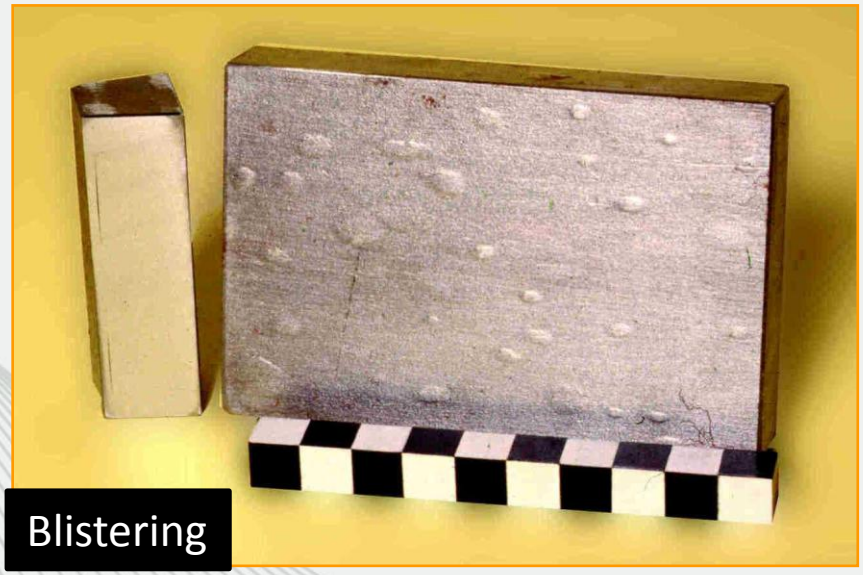



- Accumulation of hydrogen in the defect
- Increase of the pressure
- Mechanical rupture: formation of cracks and blister

# HIC, SOHIC, SWC: the “internal hydrogen”

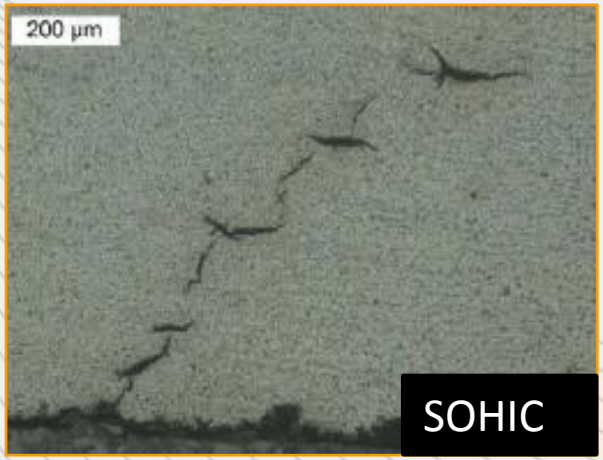



HIC



Blistering

SWC




SOHIC

# SSC, HSC: the “external hydrogen” (surface process)

- SSC: Sulfide stress cracking
- HSC: hydrogen stress cracking

Also referred as hydrogen embrittlement

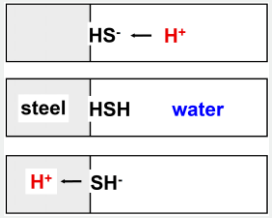
Requirement:

- Presence mechanical solicitation
- Presence of hydrogen load in service
- Possible presence of “catalyser”: $H_2S$, $H_3As$,HCN…

# SSC, HSC: the “external hydrogen” (surface process)

Insertion of dissociated hydrogen (proton + $e^-$) in the metal

- Because of an electrochemical hydrogen load (cathodic polarization)
- Because of the presence of “proton transfer catalyzer” such as $HS^-$




Strong perturbation of the crystallographic network, creation of local stress.

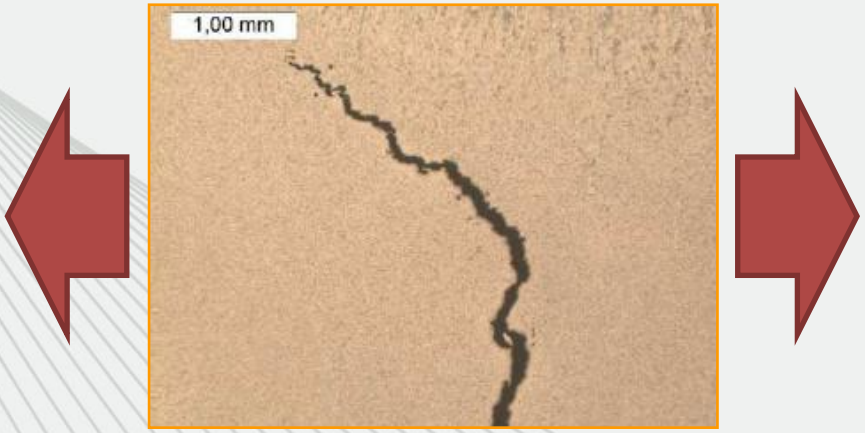
Mechanical load + local stress: nucleation of cracks:

- Starting from the surface
- perpendicular to the main stress axis
- below the elasticity limit.

# SSC, HSC: the “external hydrogen” (surface process)

Sensitive material: usually high-strength steels (Typically for yield tensile stress around 1000MPa and above)

The material recover its initial properties if the hydrogen load stop (and if there are not yet cracks)



# Hydrogen loading

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# Hydrogen loading

**Hydrogen load during the exploitation of the material**

- Off-shore structure: Structure pieces under cathodic protection
- Oil and gas: Pipes and tanks for oil crudes storage and transport
  - Acidic environment: hydrogen evolution due to corrosion mechanism
  - Impurities with catalytic effect (hydrogen sulfur, cyanide,..)

**Hydrogen load during the fabrication of the material**

- Contamination during fabrication processes:
  - Treatments: carbonizing, cleaning, pickling, phosphating, electro-plating…
  - Fabrication: roll forming, machining and drilling (lubricant effect, welding) or brazing

**Thermal or other treatments to remove internal hydrogen**

# How to detect and study hydrogen embrittlement

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# Total hydrogen measurement in alloy

Very difficult due to the high diffusivity of hydrogen

Very fast unload

**Indirect measurements**

# Measurement and study of hydrogen damage

**Inspection (non destructive)**: all the techniques allowing to detect cracks
(ultrasound based techniques, radiography, acoustic emission, eddy current…

**Mechanical test and/or metallography (destructive)**

**Deep study of mechanism:** permeation on thin metallic membrane (heavy technique)

Strong interest in assessing hydrogen embrittlement **sensitivity**

# Assessment of the hydrogen embrittlement sensitivity

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# Hydrogen induced cracking (HIC)

# NACE TM0284 test

Objective of the test: susceptibility of different grades of steels to the HIC in a short time

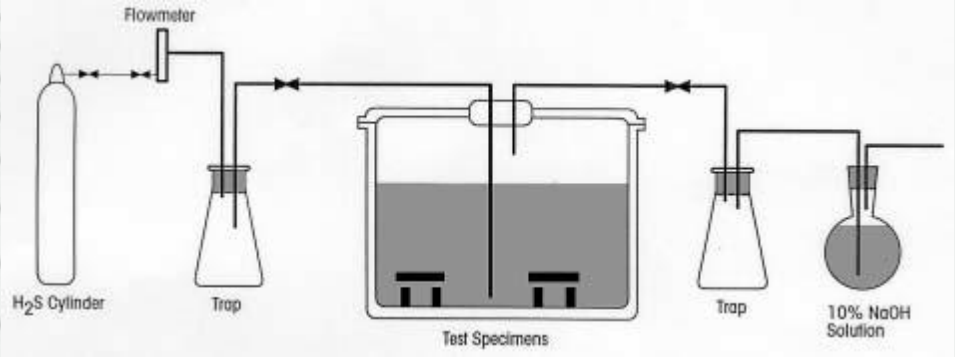
Test solution

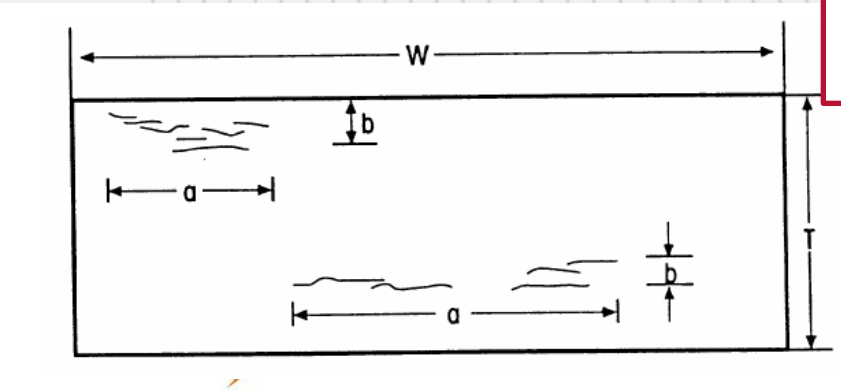
5% NaCl y 0.5% CH3COOH saturated with H2S

Synthetic water (standard ASTM D1141) saturated with H2S

Test duration

96 hours




Parameters determination

CSR = Σ(axb)x100/(WxT)

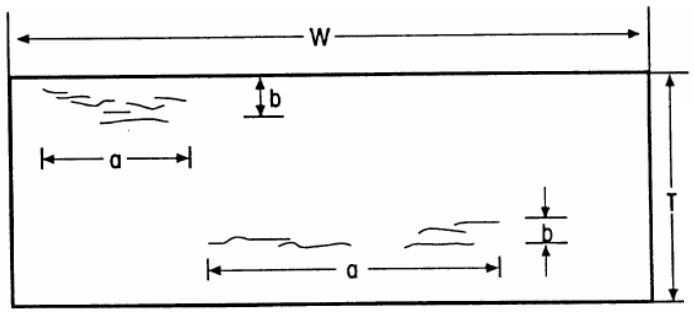
CLR = Σax100/W

CTR = Σbx100/T

CONFIDENTIAL

# NACE TM0284 test

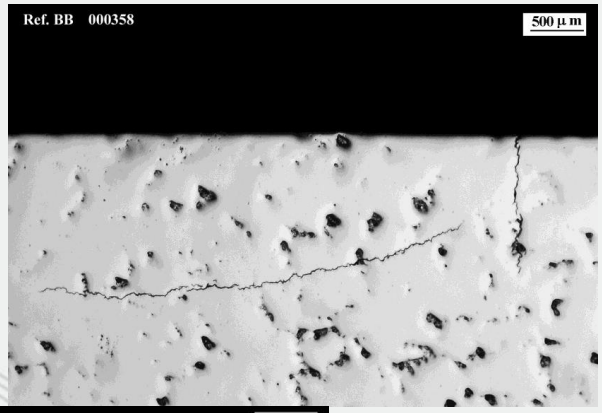
Objective of the test: susceptibility of different grades of steels to the HIC in a short time

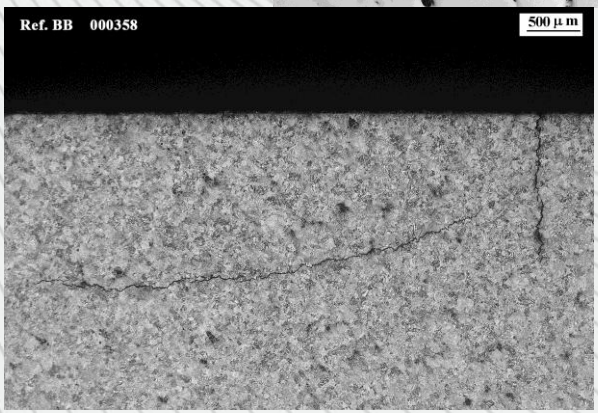



**CSR = Σ(axb)x100/(WxT)**

**CLR = Σax100/W**

**CTR = Σbx100/T**




Muestra/*Sample* 1:

| Sección /Section | CLR | CTR | CSR |
|---|---|---|---|
| A | 3,500 | 39,000 | 1,365 |
| B | 32,000 | 27,650 | 5,058 |
| C | 17,900 | 22,400 | 4,010 |
| Media/Mean | **17,800** | **29,683** | **3,477** |

Muestra/*Sample* 2:

| Sección /Section | CLR | CTR | CSR |
|---|---|---|---|
| A | 8,867 | 4,400 | 0,390 |
| B | 13,500 | 9,550 | 0,433 |
| C | 20,800 | 1,900 | 0,395 |
| Media/Mean | **14,389** | **5,283** | **0,406** |

Muestra/*Sample* 3:

| Sección /Section | CLR | CTR | CSR |
|---|---|---|---|
| A | 0,000 | 0,000 | 0,000 |
| B | 0,000 | 0,000 | 0,000 |
| C | 3,033 | 37,050 | 1,124 |
| Media/Mean | **1,011** | **12,350** | **0,375** |

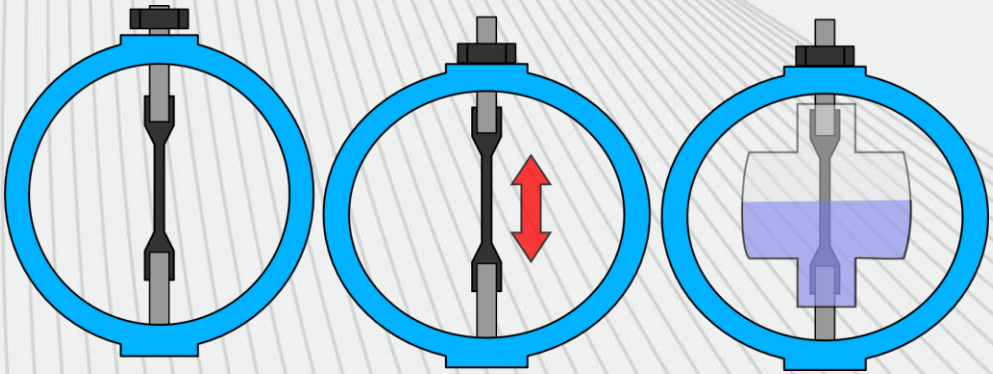
| Promedio total/ Total mean | CLR | CTR | CSR |
|---|---|---|---|
| | **11,067** | **15,772** | **1,419** |

# Hydrogen embrittlement

# NACE TM0177-method A test

Objective of the test: Evaluation of material under an uniaxial load

| | |
|---|---|
| Test medium | 5% NaCl y 0.5% $CH_3COOH$ saturated with $H_2S$ |
| Test duration | 720 hours or failure time |
| Parameters determination | Failure time<br>Presence of cracks |



Load: 75-90% of the elastic limit

# NACE TM0177-method A test

Objective of the test: Evaluation of material under an uniaxial load

Coupon

Coupon after failure

Setup

# Slow strain rate technique (SSRT)

# SSRT

Objective of the test: material resistance evaluation under a constant slow elongation and in an aggressive medium

**Test solution**

- **5% NaCl y 0.5% $CH_3COOH$ saturated with $H_2S$**
- **Synthetic water and cathodic polarization**

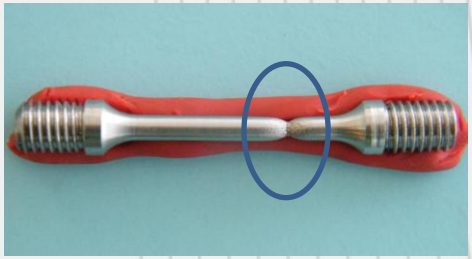
**Or tailored medium**

**Test duration**

- **Depends on the material tested (Optimization of the elongation speed)**

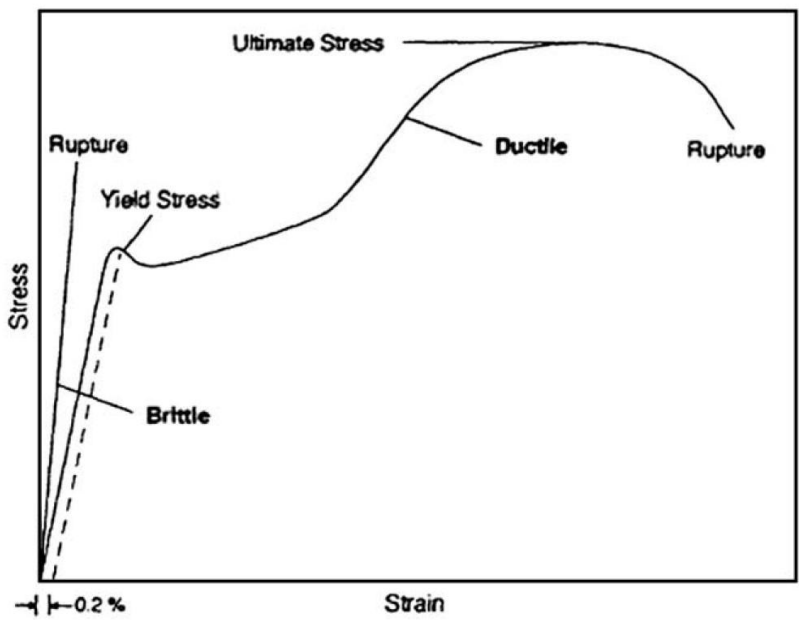
**Parameters determination**

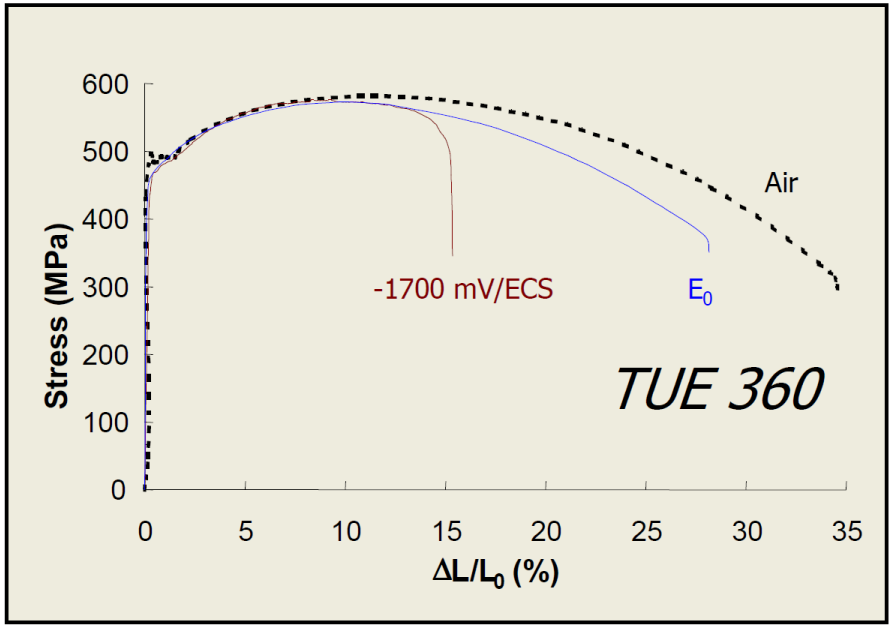
- **Area reduction ratio**
- **Failure time**
- **Presence of cracks**



# SSRT

Objective of the test: material resistance evaluation under a constant slow elongation and in an aggressive medium



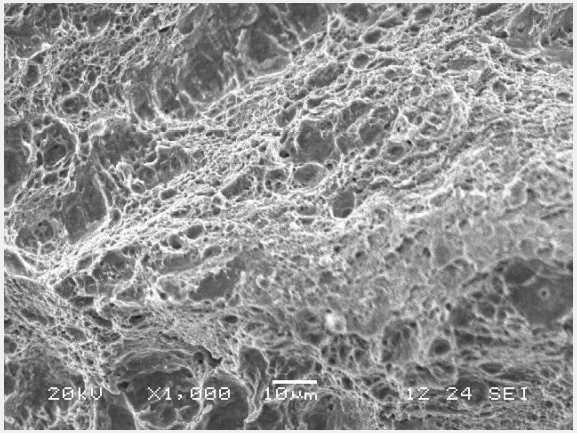




Separation of the failure coming from :

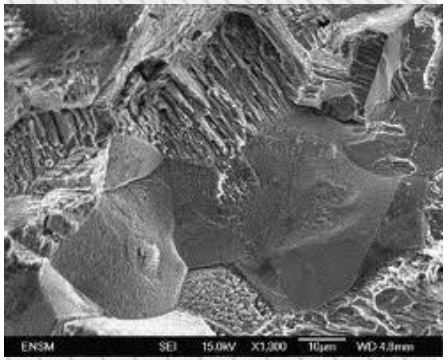
- Mechanical solicitation
- Corrosion damage
- Hydrogen embrittlement

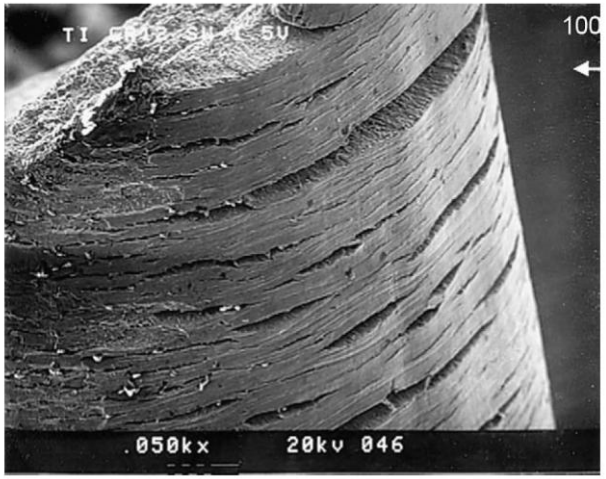
Objective of the test: material resistance evaluation under a constant slow elongation and in an aggressive medium

Ductile




Fragile



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