Hydrogen embrittlement of steels.

San Sebastián Workshop
March 18th, 2014
- Hydrogen damage
- Hydrogen damage and steel
- Hydrogen loading
- How to study hydrogen embrittlement
- Assessment of the hydrogen embrittlement sensitivity
Hydrogen damages
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\textsuperscript{th} century)

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

Hydrogen damage

- Hydrogen environment embrittlement (HEE)
- Hydrogen stress cracking (HSC)
- Loss in tensile ductility
- Degradation of other mechanical properties

- Porosity
- Blistering
- Shatter flakes, fish eyes
- Hydrogen attacks
- Creation of internal defect
- Solid solution hardening
- Hydrogen embrittlement
- Slow strength rate embrittlement
- High strength rate embrittlement
- Hydride embrittlement
Hydrogen damage

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 ??
Hydrogen damage

Hydride embrittlement

High strength rate 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 ??

Hydride forming with metals like titanium, zirconium and vanadium
Hydrogen damage

Porosity
Blistering
Shatter flakes, fish eyes
Hydrogen attacks
Creation of internal defect

Relevant for steel

Relevant for steel
Hydrogen damage

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 ??
Hydrogen damage and 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 $CH_4$

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

Delay
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”

- Accumulation of hydrogen in the defect
- Increase of the pressure
- Mechanical rupture: formation of cracks and blister
HIC, SOHIC, SWC: the “internal hydrogen”
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”: $\text{H}_2\text{S}$, $\text{H}_3\text{As}$, $\text{HCN}$…

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
Hydrogen loading

- 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,...)
- 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
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
Hydrogen induced cracking (HIC)
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:
- $CSR = \sum (axb) \times 100/(W \times T)$
- $CLR = \sum ax \times 100/W$
- $CTR = \sum bx \times 100/T$
NACE TM0284 test

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

\[ CSR = \frac{\Sigma (axb) \times 100}{W \times T} \]
\[ CLR = \Sigma ax100/W \]
\[ CTR = \Sigma bx100/T \]

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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$_3$COOH saturated with H$_2$S
- **Test duration**: 720 hours or failure time
- **Parameters determination**:
  - Failure time
  - 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)
Objective of the test: material resistance evaluation under a constant slow elongation and in an aggressive medium

Test solution
- 5% NaCl y 0.5% CH₃COOH saturated with H₂S
- Synthetic water and cathodic polarization

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

Parameters determination
- Area reduction ratio
- Failure time
- Presence of cracks

Or tailored medium
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
Thank to Marta Tejero