"POLITEHNICA" UNIVERSITY OF TIMIŞOARA

Department of MATERIALS and MANUFACTURING ENGINEERING

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HYSULFCEL

Production of Hydrogen from Black Sea Water using Fuel Cells based on Hydrogen Sulfide

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Study of The Influence of Hydrogen Sulfide upon Materials Used on Equipment for Hydrogen Storage

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1. Effect of H_2S upon steels

Direct effect

- ❑ Anodic dissolving ← slight ***acid*** character (dissolved in H_2O)
- ❑ Inhibiting effect on corrosion ← passivizing layer FeS

Layer composition *disputed* (depending of concentration in H_2S)

- ➢ **Pyrite** (FeS_2 – cubic crystallization system)
- ➢ **Troilite** (FeS – hexagonal crystallization system)
- ➢ **Kansite** (Fe_9S_8)
- ➢ **Pirhotite** ($Fe_{(1-x)}S$, x = 0 … 0.2)
- ➢ **Mackinawite** ($(Fe,Ni)_{1+x}S$, with x = 0 … 0.11), tetragonal crystallization)

Direct effect of H_2S upon steels

Effect of anti-corrosive protection

⇨ 3 parameters:

- **pH level** of aqueous environment
- **Concentration** in H_2S of solution (acts like electrolyte)
- **Time** of immersion of iron-based components

Direct effect of H_2S upon steels

pH level of aqueous environment

- Predominant opinion: 1st component on corroded surface is *mackinawite* (metastable)
- Changes to stable form: *troilite* and *pyrite*.

Direct effect of H_2S upon steels

Mechanism of transformation in acid H_2S solutions

- $Fe + H_2S + H_2O \leftrightarrow FeSH_{ads} + H_3O^+$ (1)

‡

The compound FeSH adsorbed in the surface subject to corrosion:

- $FeSH_{ads} \leftrightarrow Fe(SH)_{ads} + e^-$ (2)
- $Fe(SH)_{ads} \rightarrow FeSH^+ + e^-$ (3)

Reaction product $FeSH^+$ - incorporated directly on corroded surface into the *mackinawite* layer :

- $FeSH+ \rightarrow FeS_{1-x} + xSH^- + (1-x)\ H^+$ (4)
-

Direct effect of H_2S upon steels

Another possibility : hydrolysis ⇨ separation of Fe^{2+}

- $FeSH^{+} + H_3O^{+} \leftrightarrow Fe^{2+} + H_2S + H_2O$ (5)

Reaction (4) determines:

- local saturation
- local germination &
- development of one or more iron sulfides (*mackinawite* or *troilite)*

Direct effect of H_2S upon steels

Anodic process depending on the pH-level:

pH < 2

- Reaction (5) &
- Small quantities of sulfide forms

(relatively higher solubility of FeS phases)

Direct effect of H_2S upon steels

pH = 3…5

- H_2S inhibiting effect
- $FeSH^+$ ⇨ partially *mackinawit* - reaction (4).
- *mackinawite* could change to *troilite*

(higher stability & better protecting properties).

Direct effect of H_2S upon steels

pH ≥ 5

- only *mackinawite* as reaction product
- protection property of *mackinawite* is lower ⇨ inhibiting effect of H_2S ↓

Direct effect of H_2S upon steels

Concentration of H_2S

- ↑% H_2S generate ⇨ *kansite* (many structural defects) ⇨ poor protection to corrosion for Fe

  (less than *pyrite* or *troilite*)
- ↑% H_2S ⇨ deposition of *mackinawite* on corroded surface (layer adherent) ⇨

  NO inhibition effect on corrosion.

Direct effect of H_2S upon steels

SSC = „*sulfide stress cracking*"

Under combined effect

- Environmental factors
- Tensile stress conditions

! Promoted by high density of defects

(heat treatments, cold deformation etc.)

! Steels require both ↑Rm + ↑K

Direct effect of H_2S upon steels

SSC caused by atomic H

- H adsorption in the presence of sulfides FeS.
- Atomic H diffuses inside metal ⇨ fragility, sensitization to cracking

Predisposed to SSC.

- High resistance metallic materials
- Hard areas within welded joints (HAZ)

Direct effect of H_2S upon steels

Exemple

Steel tubes transporting products containing H_2S

HRC > 22 (σ_c > 550 MPa)

- ↑sensibility to SSC
- corrosion propagates ⊥ to load (inter-granular or trans-granular cracks)

HRC < 22 – soft steel

- resistant to SSC
- incipient crack are surrounded by a soft matrix
- does not promote crack propagation

Direct effect of H_2S upon steels

Ni alloying ↑ susceptibility to SSC

- H_2S in presence of Ni delays recombination of H atoms to molecular state of gaseous H ⇨ diffusion of H in steel
- Cracking is caused by *hydrogen embrittlement* (HE)

International normative for material selection

NACE MR0175/ISO 15156 - *Non-alloyed* and *low alloyed* steels resistant to cracking and use of cast iron

- requirements & recommendations for environments containing H_2S (petrol & natural gas industry)

Example: Steel with <1% Ni - accepted:

- HRC < 22
- conditions of heat treatment:
- a) hot laminated (only non-alloyed steels)
- b) annealed
- c) normalized
- d) normalized and tempered
- e) normalized, quenched and tempered
- f) quenched and tempered

International normative for material selection

NACE MR0175/ISO 15156 - *Non-alloyed* and *low alloyed* steels resistant to cracking and use of cast iron

Example: Welded joint

- Heat Affected Zone (HAZ) – max. 250 HV
- Heating temperature for post-welding treatment – min. 620 °C
- Limitations to the filling material

International normative for material selection

NACE MR0175/ISO 15156 - *Corrosion resistant alloys* and *other alloys*

- Transport or process fluids containing hydrogen sulfide:
- Materials
  - Austenitic stainless steels
  - Nickel-based alloys,
  - Ferritic stainless steels,
  - Martensitic stainless steels,
  - Duplex stainless steels,
  - Precipitation hardening steels and Ni-based alloys,
  - Alloys based on Co, Ti, Ta, Cu, Al

Indirect effect of H_2S upon steels

Connected with formation of atomic H:

- $H_2S \rightarrow 2H^+ + S^{2-}$
- $Fe + 2H^+ \rightarrow Fe^{++} + 2H^0$ (6)
- $2H^0 \rightarrow H_2$

H is produced at the anode of a *galvanic micro-cell* at the same time with the formation of FeS

Effect of interaction of H with steels

Attack Type	Environment	Type of Material Degradation	Prevention Methods
Hydrogen attack	T> 230°C, Pressure H_2 >7 atm	Decarburizing; Cracking; Significant reduction of strength	Selection of appropriate alloys
Formation of blisters ("hydrogen blistering")	T> 100°C, presence of H_2S, Accentuated by cyanides	Blisters, when the defect is superficial; Cracks for profound defects	Protection depositions; Selection of appropriate materials
Embrittlement in the presence of hydrogen	T> 100°C, presence of H_2S, Accentuated by cyanides	Significant reduction of ductility	Similar with „hydrogen blistering"
Cracking in the presence of hydrogen	At ambient temperature, as effect of rapid cooling, similar with hydrogen attack	Significant reduction of ductility; Increase of cracks	Selection of appropriate materials

Hydrogen attack

- Presence of atomic H (decomposition of H_2S)
- $T > 230^{o}C$, $p_H > 7$ atm

$$Fe_3C + 4H \longrightarrow 3Fe + CH_4 \quad (7)$$

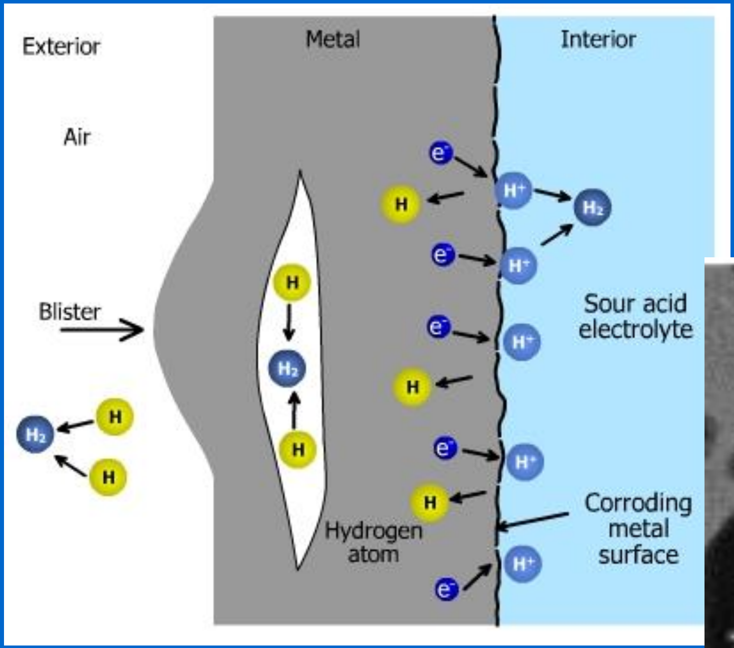
- Local decarburization ⇨ ↓Rm
- Blisters of CH_4 methane (not H)
- Prevention - using stabilized steels

Hydrogen blistering

Process:

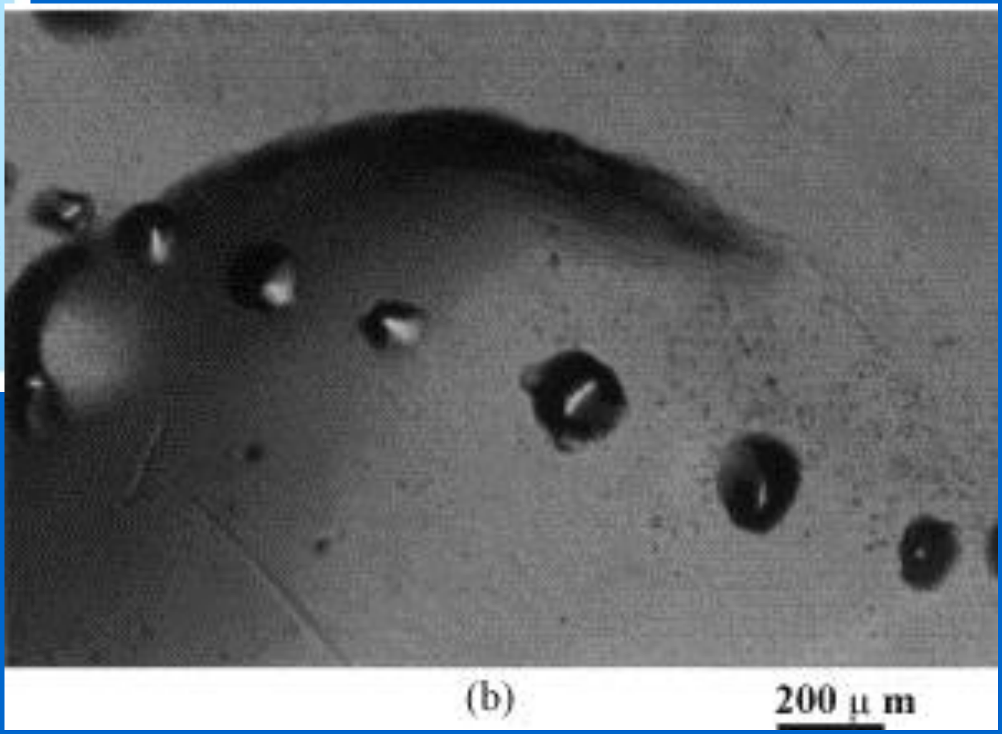
- H diffusion inside the steel
- H caption by a non-metallic inclusion or at grain limits
- Producing molecular H (cannot diffuse) ⇨ localized in gaseous state (↑↑p) ⇨ pores (blisters) & cracks
- Cracks -parallel with the surface, on the sheet's lamination direction at different depth.
- Interconnected cracks leading to material destruction.

Hydrogen blistering



Blistering process

Formation of blisters



Hydrogen embrittlement

- H.E. = ↓↓A of steel in the presence of H
- H atom << Fe → migrate into Fe lattice
- Reside *interstitially* between the individual metal atoms → amplify $\boldsymbol{\sigma}$ of applied forces
- Catastrophic fracture for $\boldsymbol{\sigma} \ll \boldsymbol{\sigma}_C$
- Susceptible -
  - Hardened steels (HRC > 40)
  - Non-alloyed steels

Steel cracking in the presence of H

HSC – H stress cracking *or* HIC – H induced cracking *or*

"static fatigue"

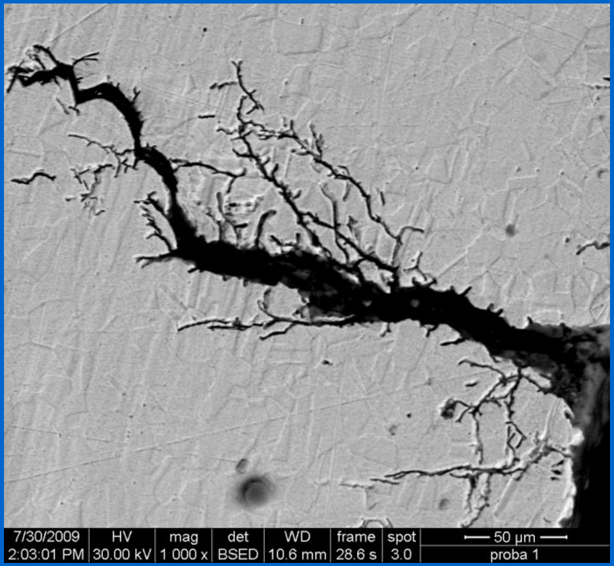
- Similar with fatigue fracture
- At $\sigma < \sigma_C$
- Similar to fatigue fracture has a limit σ_{HIC} ($\sigma < \sigma_{HIC}$) fracture does NOT propagate

Steel cracking in the presence of H

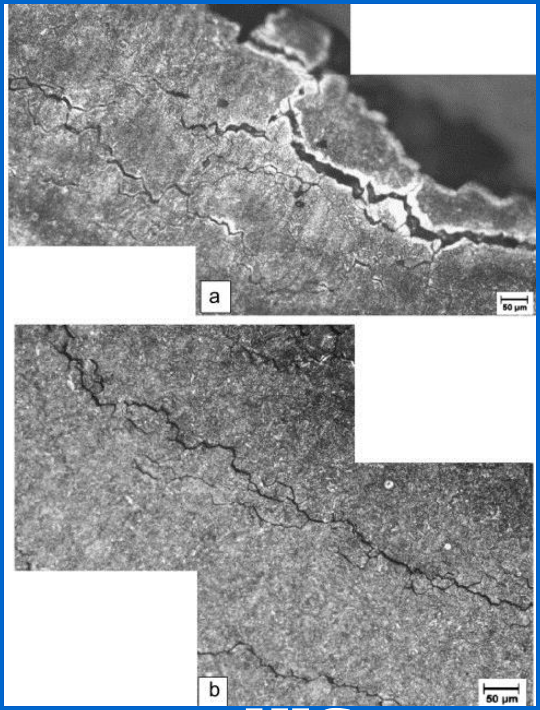
2 stages (similar with fatigue fracture)

- H absorption - H diffuses regions with ↑σ
- Brittle fracture - single crack, with a smooth breaking surface

UNLIKE stress corrosion cracking SSC – multiple cracks



SSC



HIC

Steel cracking in the presence of H

Another difference between SSC and HIC

- SSC propagates ⊥ to surface
- HIC propagates ∥ to surface

Aggravating of HIC: .atomic H accumulates at grain limits and nonmetallic inclusions

SSC HIC

Effect of H_2S upon Al

- No effect on Al till 500°C (dry/wet)
- No significant effect in $H_2S + NH_3$
- Lower resistance at H_2S + 30–50% CO_2
- Differences between alloys

Alloys	Temperature	
	49°C	71°C
3003	0.05	0.01
5052	0.05	0.01
6061	0.05	1.1

Dissolution speed in $H_2S + NH_3$ solutions (mm per year).

Effect of hydrogen on Al

- Dry gaseous H has NO negative effect on Al
- H blistering – only on melting & heat treating (reaction with H_2O vapors)

Effect of H on Cu and its alloys

Only when Cu or Cu alloy contains O

- $Cu_2O + 2H = 2Cu + H_2O$ (g)

H diffuses inside the Cu

reacts with O (solid solution or oxides) and forms water (cavities).

Effect of H on Ti and its alloys

1. Formations of Titanium hydride (βTi) - (high concentration of H)
2. Embritlement at plastic deformation

   (cpTi more sensitive than pure Ti)
3. Embritlement at impact (α/βTi, βTi)

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