# **Corrosion of passive metals**

# Jacek Banaś



University of Science and Technology (AGH-UST) Faculty of Foundry Engineering Department of General and Analytical Chemistry

#### Effect of chemical composition on passive behaviour of the alloy



Stationary polarization curves of austenitic Fe-Cr-Ni alloys in 1M  $H_2SO_4$ 



Model of passive film on pure chromium

Stationary polarization curves of Fe-Si alloys in 1M H<sub>2</sub>SO₄

% Cr	Structure of passive film	thickness A
0	well oriented spinel	36
5	well oriented spinel	27
12	weak oriented spinel	21
19	mainly amorphous	19

Effect of chromium on the structure of passive film on Fe-Cr alloys in neutral aqueous solutions J.Kruger in Passivity of Metals, ed.by Electroche. Soc. Inc. Princetown ,N. Jersey 1978



### Effect of chemical composition on passive behaviour of the alloy



#### **Corrosion of passive alloys**



**Stress corrosion** 





Pitting corrosion



#### **Crevice corrosion**



Inergranular corrosion

**Corrosion-erosion degradation** 

#### **Pitting corrosion**



Mechanism of pitting corrosion in chloride containing media



Pitting corrosion of iron in atmosphere polluted with SO<sub>2</sub>

#### Pitting corrosion





Schematic of a polarization curve showing critical potentials and metastable pitting region. EP, pitting potential; ER, repassivation potential; Ecorr, corrosion potential.

Autocatalytic process occurring in a corrosion pit. The metal, M, is being pitted by an aerated NaCl solution. Rapid dissolution occurs in the pit, while oxygen reduction takes place on the adjacent metal surfaces.

#### **Pitting corrosion**





#### Pitting corrosion of Ti in CH<sub>3</sub>OH-LiCl solutions

Pitting corrosion of Fe-18%Cr alloy in CH3OH- $H_2SO_4$  solutions



Corrosion of heat exchanger (carbon steel) in water

#### Effect of molybdenum on stability of passive film on stainless steels

(a)  

$$\begin{array}{c}
-OH - M - OH_{2^{+}} - - - A^{-} \\
-M - OH \\
-OH - M - OH_{2^{+}} - - - A^{-} \\
-M - OH \\
-OH - M - OH_{2^{+}} - - - A^{-} \\
-M - OH \\
-OH - M - OH_{2^{+}} - - - A^{-} \\
-M - OH \\
-OH - M^{+} - M_{0}O_{4}^{2} - - - C^{+} \\
-M - OH \\
OH - M^{+} - M_{0}O_{4}^{2} - - - C^{+} \\
-M - OH \\
OH - M^{+} - M_{0}O_{4}^{2} - - - C^{+} \\
-M - OH \\
OH - M^{+} - M_{0}O_{4}^{2} - - - C^{+} \\
-M - OH \\
-M -$$

Adsorption of ions on hydrous metal oxide surface which provides the fixed charge whose determines the ion selectivity of the membranes.

(a) anion- selective, (b) cation- selective membrane[53].

#### Inergranular corrosion







Inergranular corrosion of NIROSTA 2202 steel (22%Cr,6%Ni,3%Mo) in 93.5 wt.%  $H_2SO_4$  (100°C)

#### Stress corrosion cracking



**Crack velocity:** 

$$v = \frac{D_s}{L} (e^{\sigma a^3/kT} - 1)$$

 $D_{s}$  – surface self diffusion coeficient L – diffusion length  $\sigma$ – elastic surface stress at the crack tip  $a^3$  – volumen of vacancy

Surface mobility model of Stress corrosion cracking (SCC) according to Galvele J.R. Galvele, Corrosion Science 27,1 (1987)

# The effect of H<sub>2</sub>S on hydrogen embrittlement

HIC – hydrogen induced cracking,

occurs in low- and high-strength steels even without external stress. Crack propagation proceeds paralell to surface.



SSCC – sulphide stress corrosion cracking,

occurs in high-strength steels.

Crack propagation proceeds perpendicular to surface.



# The effect of H<sub>2</sub>S on hydrogen embrittlement



HIC and HISCC of pipelines after 10 years exploitation in natural gas containing 4.5%  $H_2S$ .

### Hydrogen embrittlement



Mechanism of hydrogen embrittlement by stress iduced hydride formation.

# Hydrogen embrittlement

