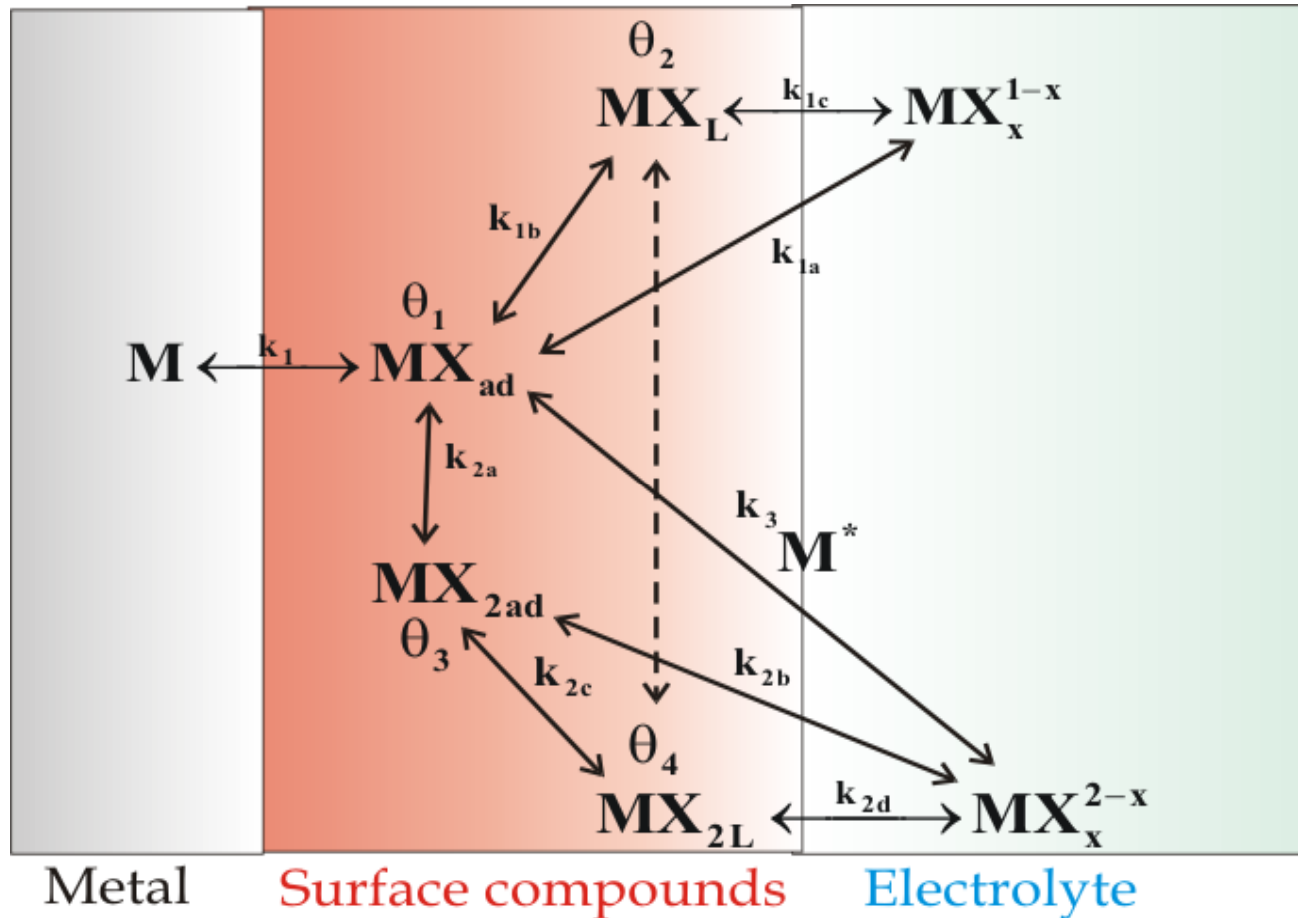# Corrosion in active state

Jacek Banaś

J. Banaś, Corrosion Resistant Alloys. Fundamental Aspects of Material Selection, in Metallurgy on the Turn of the 20th Century, ed. Committee of Metallurgy of the Polish Academy of Science, Kraków 2002,pp. 89-112

Mechanism of corrosion in active state

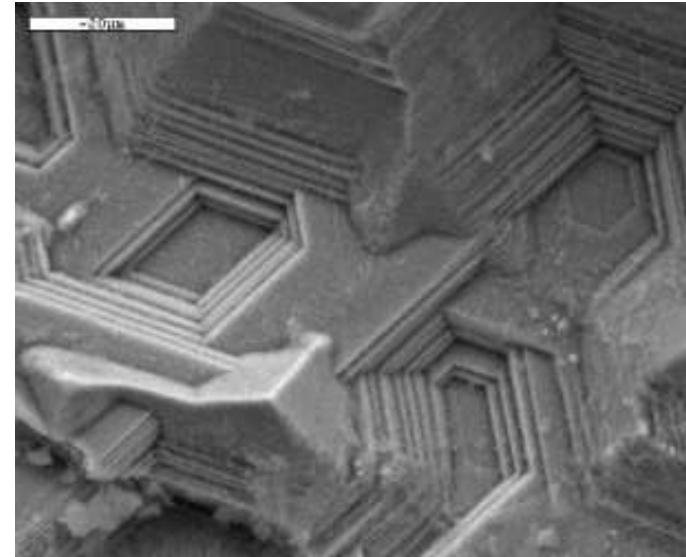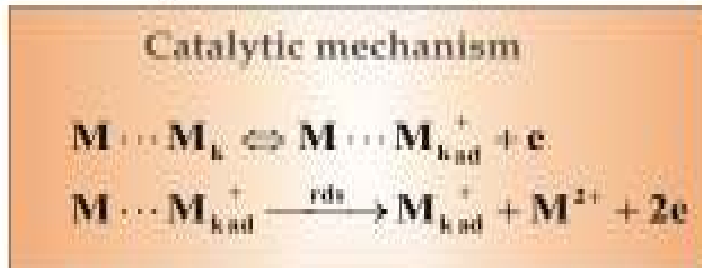Mechanism of electrochemical corrosion of divalent metal in electrolyte containing solvating anion X^{-x}
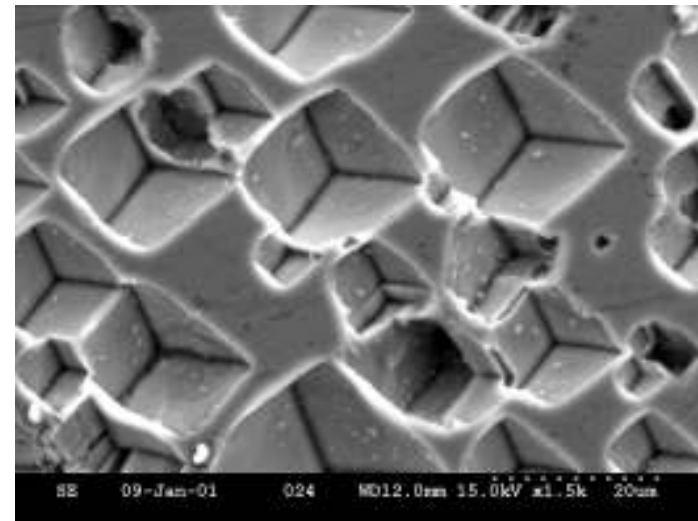
Mechanism of corrosion in active state

Consecutive mechanism

$$M \Leftrightarrow M^+_{ad} \xrightarrow{rds} M^{2+} + e \rightarrow M^{n+} + (n-2)e$$

Bond strength of metal lattice

Dielectric permittivity of the solvent

Catalytic mechanism

$$M \cdots M_k \Leftrightarrow M \cdots M^+_{k\,ad} + e$$

$$M \cdots M^+_{k\,ad} \xrightarrow{rds} M^+_{k\,ad} + M^{2+} + 2e$$

The influence of metal structure and solvent properties on the mechanism of anodic dissolution of metal.

SEM micrograph of (0001)Zn surface after anodic etching in $CH_3CN - 0,1$ $LiClO_4$ (-0,142V).

SEM micrograph of (111)Al surface after anodic etching in DMF $- 0,1$ LiCl (1,5 V).

Dissolution of alloys

For the binary AB alloy the equilibrium potentials E_A and E_B of the components can be expressed as follow:

$$E_A = E_A^0 + \frac{RT}{aF} ln \frac{a_{A^{a+}}}{a_A}$$

E_A^0 and E_B^0 are the standard potentials of the components

$$E_B = E_B^0 + \frac{RT}{bF} ln \frac{a_{B^{a+}}}{a_B}$$

Equilibrium between the alloy phase and the solution is reached when the potential of the components are equivalent: $E_A = E_B$

$$exp \frac{F}{RT}(E_A^0 - E_B^0) = \frac{a_{B^{b+}}^{1/b} \cdot a_A^{1/a}}{a_{A^{a+}}^{1/a} \cdot a_B^{1/b}}$$

Composition of the alloy determines specific composition of the electrolyte during alloy dissolution. The composition of the solution depends on the difference of standard potentials of the components

K.E. Heusler: Metalurgia i Odlewnictwo 16, 1, 5 (1990)

Dissolution of alloys

The increase of the anodic potential of the electrode surfaces with respect to the equilibrium potential stimulates selective dissolution of more active component (component with the lower standard potential). The selective corrosion of alloys containing the components with significant difference of standard potentials can be observed in the praxis. Copper-zinc brasses, copper aluminum bronzes undergo "dealloying" in many aggressive environments.

The dissolution rate " j_i " of the component "i" of multi-component alloy can be expressed by the equation:

$$j_i = n_i \cdot F \cdot k_i \cdot y_i^s$$

where k_i is the rate constant and y_i^s is the surface fraction of the component "i".
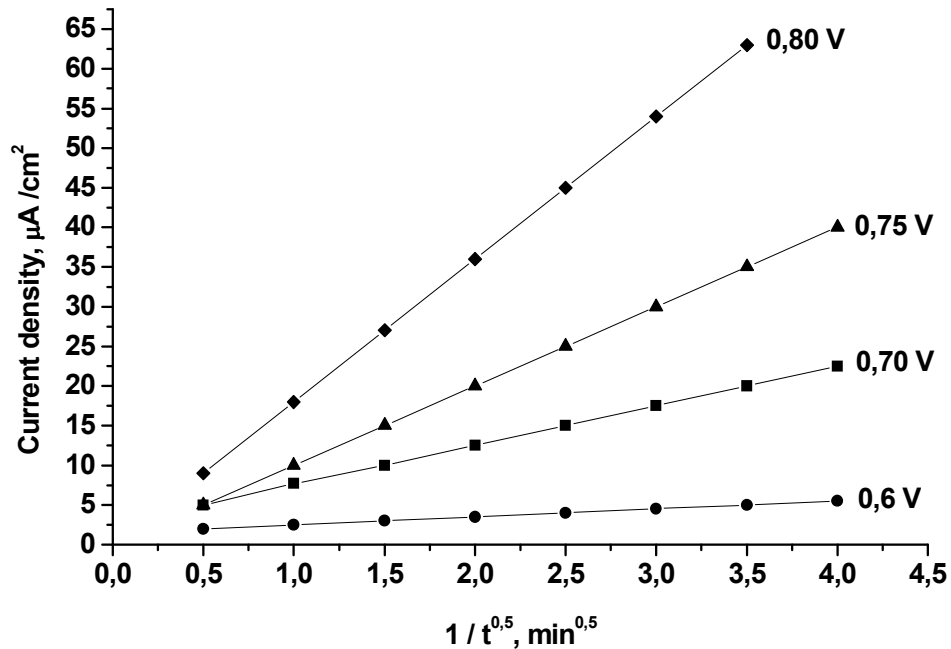
The total dissolution current is the sum of the partial currents of dissolving components:

$$j = \sum_i j_i$$

The dissolution current limited by the diffusion in the solid state can be expressed by the equation:

$$j_i = n_i F (y_i^s - y_i^0) \left(\frac{D}{\Pi \cdot t} \right)^{0,5}$$
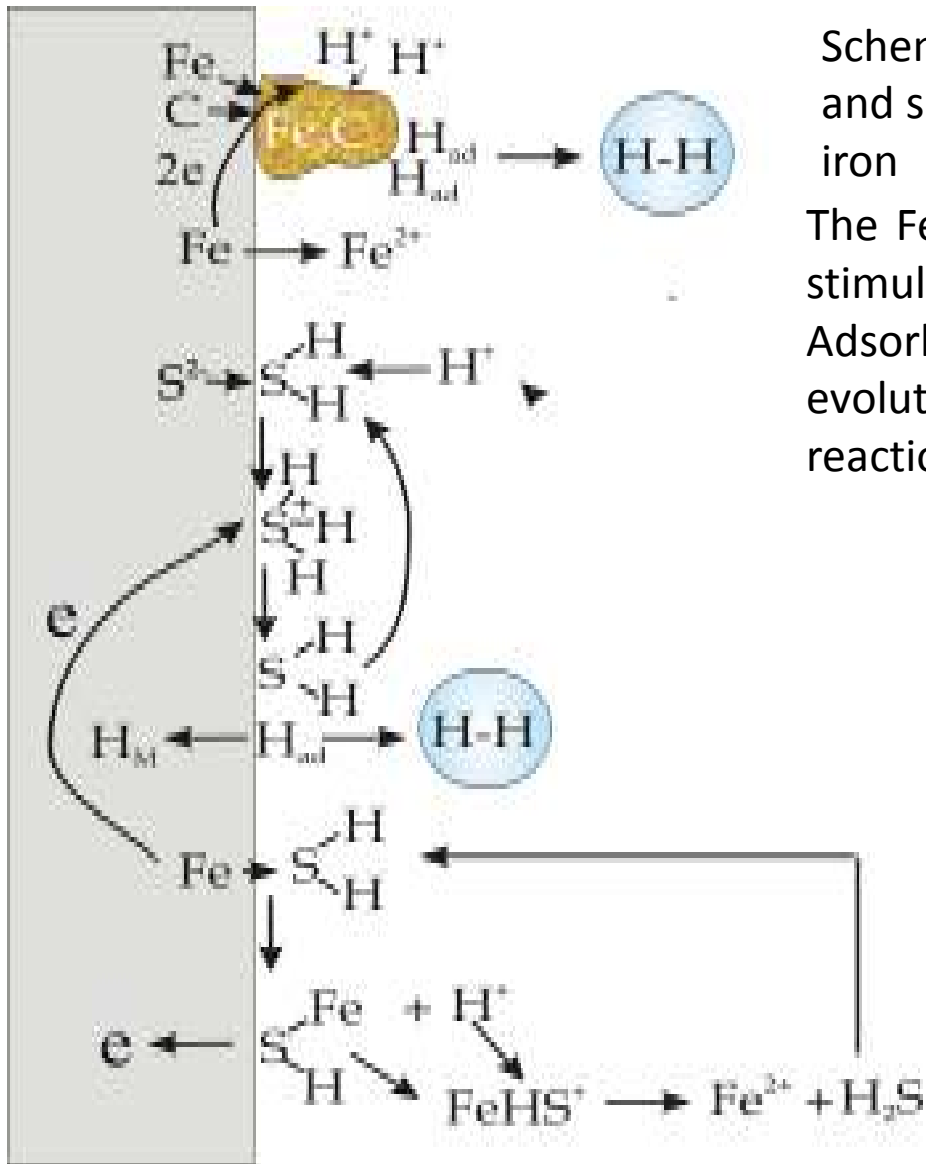
Dissolution of alloys

$$j_i = n_i F(y_i^s - y_i^0)\left(\frac{D}{\Pi \cdot t}\right)^{0,5}$$

Partial dissolution rate of Ag as a function of $1/\sqrt{t}$

for the Ag-15%Au alloy in 0,1M KNO$_3$.

The diffusion of dissolving components in the solid state can be perturbed by the grain boundary diffusion. Schwitzgebel and all [17] proposed the equation considering the contribution of the grain boundary diffusion:

$$j_i = n_i F(y_i^s - y_i^0)\left[\left(\frac{D}{\Pi \cdot t}\right)^{0,5} + \frac{const}{d}\left(\delta_{gb} \cdot D_{gb}\right)^{0,5} \cdot \left(\frac{D}{t}\right)^{1/4}\right]$$
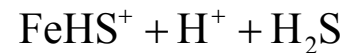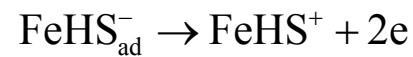
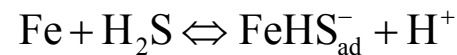H. Keiser: " Corrosion of Alloys" in "Corrosion Mechanisms" ed. F. Mansfeld, Marcel Dekker Inc. N.Y.1987

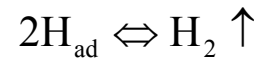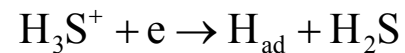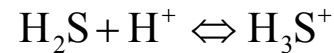# Dissolution of alloys. The effect of metaloids (C,S).

Schematic presentation of the effect of carbon and sulphur on the corrosion mechanism of iron

The Fe_3C particles act as the local cathode and stimulate micro-galvanic corrosion of the alloy. Adsorbed H_2S behaves as catalyst of hydrogen evolution and stimulates cathodic partial reaction of corrosion process.

Anodic process:

$$Fe + H_2S \Leftrightarrow FeHS_{ad}^- + H^+$$

$$FeHS_{ad}^- \rightarrow FeHS^+ + 2e$$

$$FeHS^+ + H^+ + H_2S$$

Cathodic proccess:

$$H_2S + H^+ \Leftrightarrow H_3S^+$$

$$H_3S^+ + e \rightarrow H_{ad} + H_2S$$

$$2H_{ad} \Leftrightarrow H_2 \uparrow$$

H. Bala: : Metalurgia i Odlewnictwo 16, 1, 97 (1990)
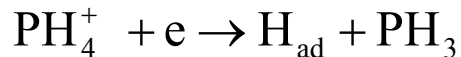
Dissolution of alloys. The effect of metaloids (N,P).

Corrosion inhibition can be observed in the presence of nitrogen and phosphorus in the metal matrix:

$$\text{Fe} - \text{P} + 3\text{H}_{ad} \rightarrow \text{Fe}(\text{PH}_3)_{ad} \Leftrightarrow \text{Fe} + \text{PH}_3$$

$$\text{PH}_3 + \text{H}^+ \rightarrow \text{PH}_4^+$$

$$\text{PH}_4^+ + e \rightarrow \text{H}_{ad} + \text{PH}_3$$

At high concentration adsorbed PH_3 acts as inhibitor of both cathodic and anodic electrode processes. Similar effect can be observed in the presence of nitrogen in the metal matrix. Adsorbed NH_3 inhibits cathodic reaction because local alkalization of the metal surface and anodic reaction because blockes the active places (kinks, steps).

The effect of metalloid component on the corrosion of alloys is not only related to the direct inhibition or catalytic process on the metal electrolyte interface. The metalloids dissolved in the metal can change crystallographic structure of the matrix (carbon effect on martensitic transformation) and can stimulate the micro-segregation of the alloy components (C,P). These phenomena influence local composition of the alloy and defect concentration on the alloy surface and than metal corrosion.
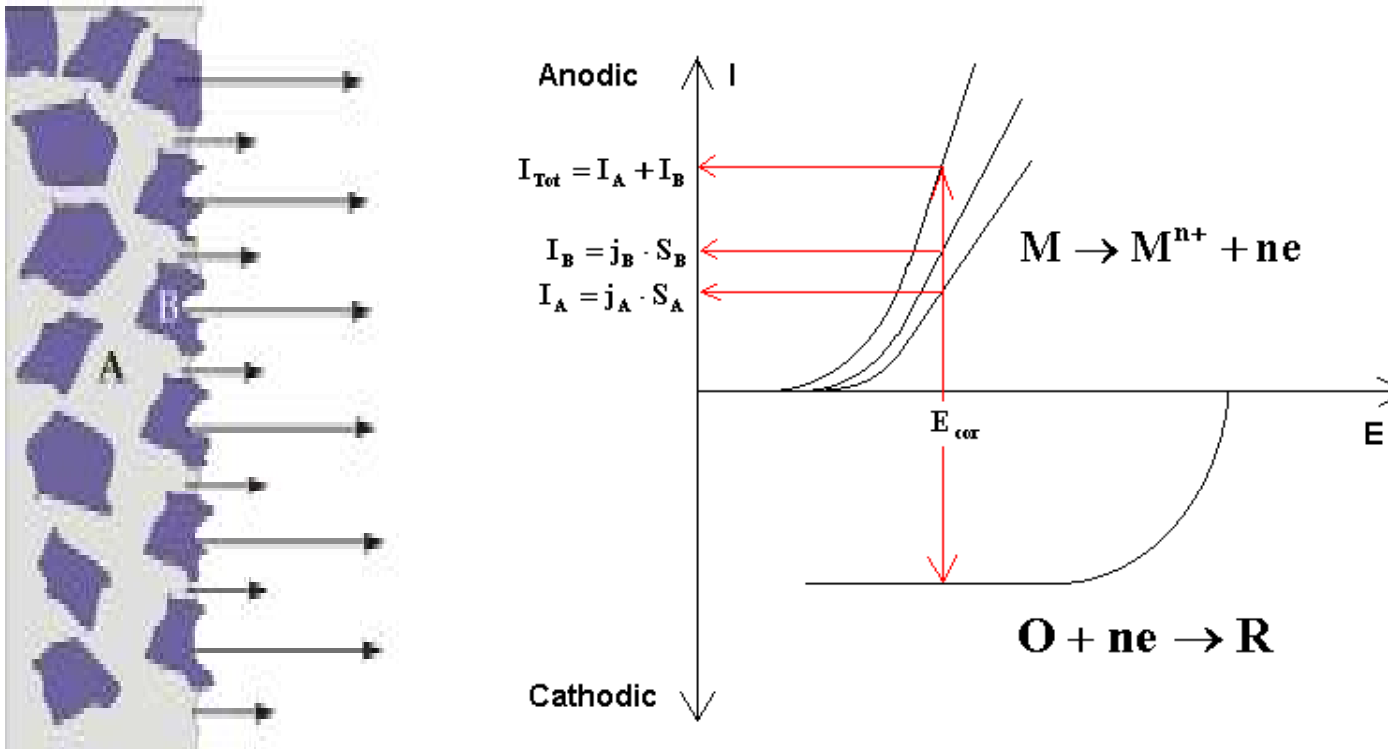
Dissolution of heterogeneous alloys
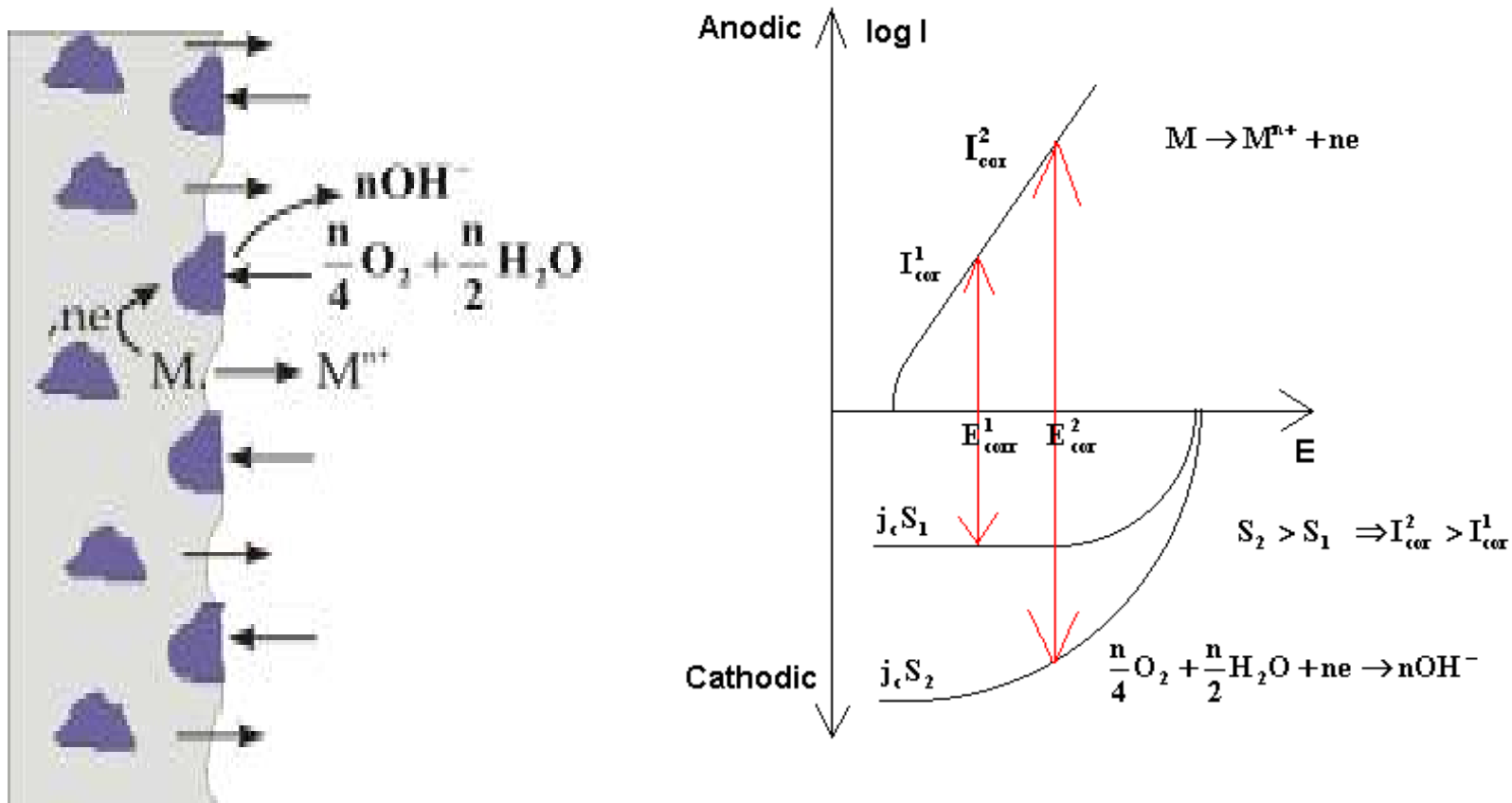
Scheme of galvanic corrosion of heterogenous alloy under stationary conditions (a) and polarization diagram of galvanic element (b) for two surface area of cathodic inclusion S_1 and S_2.
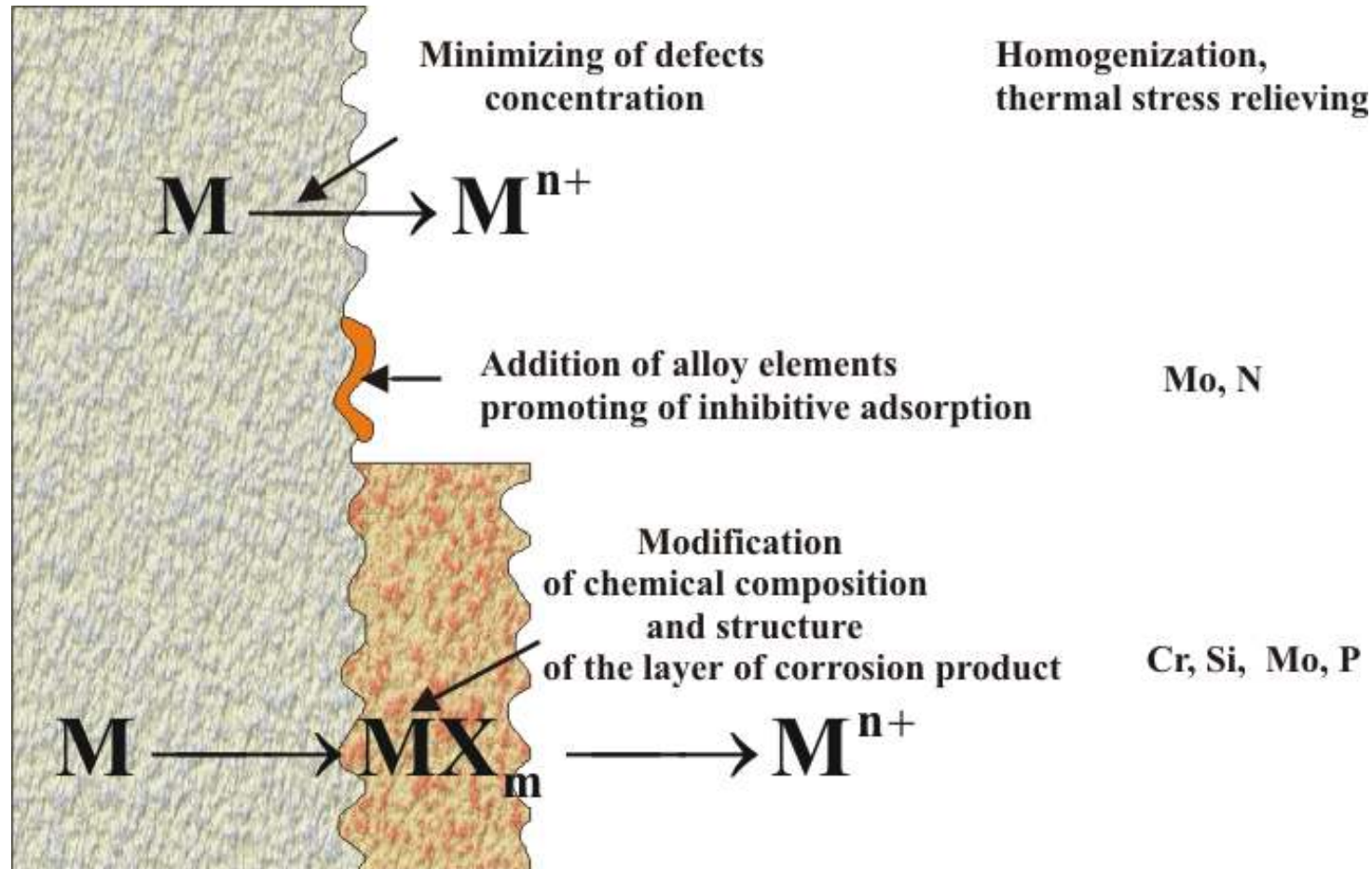
The presence of the phases with the more noble potential than the matrix stimulate their dissolution because of the action of galvanic elements matrix-inclusion.

Dissolution of heterogeneous alloys

Scheme of corrosion of heterogeneous alloy under potentiostatic conditions at the presence of strong oxidant "O" (a) and polarization diagram (b). The presence of strong oxidant "O" leads to the equalization of potential on the alloy surface.

Corrosion resistant alloys in the active state

Minimizing of defects concentration

Homogenization, thermal stress relieving

$$M \longrightarrow M^{n+}$$

Addition of alloy elements promoting of inhibitive adsorption

Mo, N

Modification of chemical composition and structure of the layer of corrosion product

Cr, Si, Mo, P

$$M \longrightarrow MX_m \longrightarrow M^{n+}$$

Schematic presentation of the factors improving corrosion resistance of active alloys

Corrosion resistant alloys in the active state

Component	Optimal content %
C	0.2 do 0.3
Solid state components	
Si	0.4 do 0.7
Mn	≤ 1.2
Ni	0.5 do 1.0
Co	≤ 0.5
Al	≤ 0.25
Carbides formers	
Cr	1.0 do 1.5
Mo	0.4 do 0.5
Ti	0.05
Nb	0.02 do 0.06
V	0.1
Modifiers	
REM (Ce)	0.1 do 0.3
AlN, VN, NbN	0.2
Impurities	
S	≤ 0.01
P	≤ 0.015
Sb	≤ 0.01
Sn	≤ 0.01
Cu	≤ 0.05
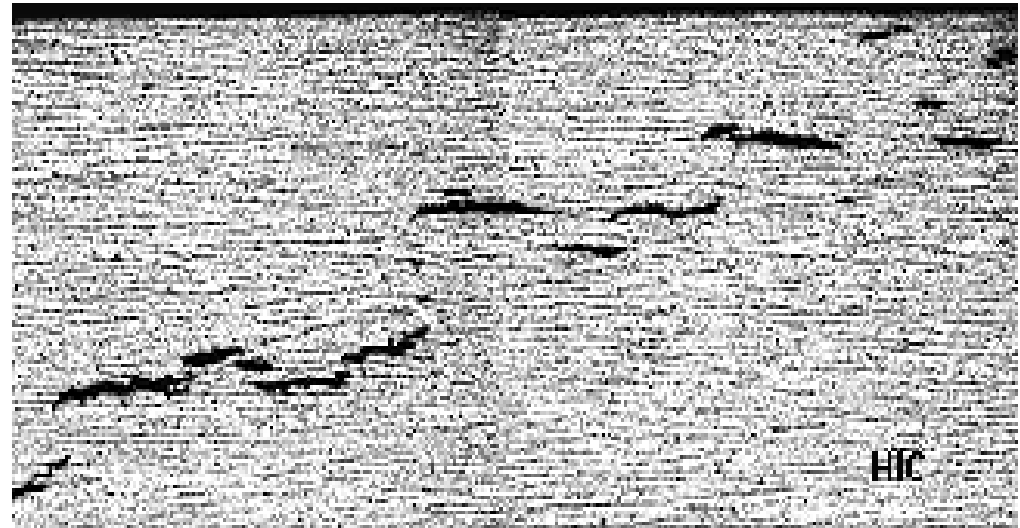
Optimal composition of carbon steel resistant
to hydrogen embrittlement

Effect of microstructure of carbon steel on the morphology of corrosion product in neutral aqueous environments