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Corrosion of Metals

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Part I

Corrosion of metals

1 Definitions

Corrosion: basic definitions

- Corrosion is a spontaneous process of metal destruction due to its physicochemical interaction with the environment
- Classification by nature of destruction:
  - local corrosion
  - uniform corrosion
- The rate of corrosion is the most important indicator
  - weight loss per time unit per unit area $\frac{\text{mg}}{\text{cm}^2 \cdot \text{day}}$
  - reduction in the thickness of the metal layer per time (mm/year)
- Classification by corrosion mechanism
  - chemical (in non-conductive media)
  - electrochemical (in conductive media)

2 Chemical corrosion

2.1 General description

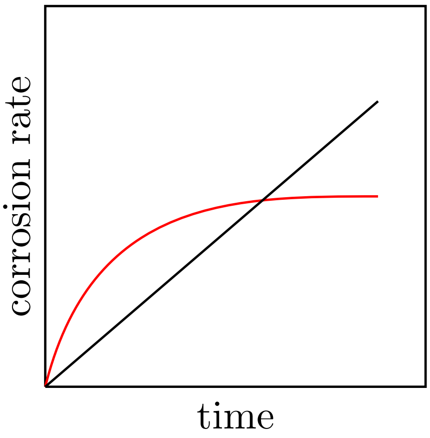
- Corrosion occurs on the place of contact of the metal with the oxidizer
  - there is no electrical current
  - corrosion products are formed on the place of contact directly
- 

  Examples:
  corrosion in gaseous environment;
  non-electrolyte solutions
  (oil)

- *A thermodynamic prediction using* ΔG, for example $3Fe_{(cr)} + 2O_{2(g)} = Fe_3O_{4(cr)}, \Delta G = -1014$ kJ
  - not all the reactions having $\Delta G < 0$ occur!
  - corrosion products can isolate metal surface
  - this prediction does not allow to estimate the rate of corrosion

2.2 Determining factors

Rate of chemical corrosion

- 

The corrosion rate is determined by the nature of the layer of corrosion products
a loose layer:
$v_{\mathrm{corr}} = kt \quad (\mathrm{Fe(OH)_3, Na_2O})$
a continuous layer:
$v_{\mathrm{corr}} = k \ln t \quad (\mathrm{Cr_2O_3, Al_2O_3})$

- Thickness of the layer: thin (under 40 nm), medium (40-60 nm), thick (more than 60 nm)

- The best protection is a continuous layer of medium thickness

- Rising of T:
  - The corrosion rate increases with the temperature by the parabolic law
  - The mechanism of corrosion can change (copper embrittlement, for example) $\mathrm{Cu_2O + H_2 \xrightarrow{T>700\ K} 2Cu + H_2O}$

3 Electrochemical corrosion

3.1 General description

- It occurs in conductive media (soil, solutions etc)
  - The oxidizer and the reductant are separated
  - just like in galvanic cell

- *A corrosion galvanic cell (or corrosion cell, CC)*
  - anode is metal (an oxidation process occurs here)
  - cathode is oxidizer (O_2, H^+, Cl_2 etc)
  - $\Delta E_{\mathrm{CC}} = E_{\mathrm{oxidizer}} - E_{\mathrm{metal}}$
  - A corrosion cell has the external circuit shorted!
- The estimation of corrosion possibility

$$\textit{if } \Delta E_{CC} > 0 \textit{ then corrosion can occur}$$

3.2 Metallic corrosion cells

- Both cathode and anode are metals
  1. two metals in different solutions ($\mathrm{Zn}|\mathrm{Zn}^{2+}||\mathrm{Cu}^{2+}|\mathrm{Cu}$)
  2. one metal in solutions of different electrolytes or in ones that have different concentrations
     ($\mathrm{Cu}|\mathrm{Cu}^{2+}, c_1 \; || \; \mathrm{Cu}^{2+}, c_2|\mathrm{Cu}, \; c_1 < c_2$)
  3. two metals immersed in one solution ($\mathrm{Fe}|\mathrm{NaCl}|\mathrm{Ni}$)
- There are examples of such CC:
  - solutions having different temperatures ($\Delta T = 10$ K, $\Delta E_{\mathrm{CC}} = 10^{-3}$ V)
  - one metal with different surface conditions (welding, forging, etc)

3.3 Processes in corrosion cell

- CC anode: oxidation of metal $\mathrm{M} - ne = \mathrm{M}^{n+}$
  - $E_{\mathrm{anode}} = E^\circ(\mathrm{M}^{n+}/\mathrm{M})$ (if the concentration is unknown)
  - $E_{\mathrm{anode}} = E^\circ(\mathrm{M}^{n+}/\mathrm{M}) + \dfrac{0.059}{n} \lg c(\mathrm{M}^{n+})$
- CC cathode: reduction of oxidizer
  - H^+ reduction is *hydrogen depolarization*
    $2H^+ + 2e = H_2$ (pH < 7)
    $2H_2O + 2e = H_2 + 2OH^-$ (pH $\geqslant 7$)
  - O_2 reduction is *oxygen depolarization*
    $O_2 + 4H^+ + 4e = 2H_2O$ (pH < 7)
    $O_2 + 2H_2O + 4e = 4OH^-$ (pH $\geqslant 7$)

- Electrode potentials (E_{cathode})
  - $E(2H^+/H_2) = -0.059\text{pH}$
  - $E(O_2/H_2O) = 1.23 - 0.059\text{pH}$
- Reminder: $\Delta E_{CC} = E_{cathode} - E_{anode}$

Secondary processes on electrodes

- Corrosion of metals at pH $\geqslant 7$ can be accompanied by forming of insoluble hydroxide

- Corrosion of zinc in acidic media without oxygen
  - C: $2H^+ + 2e = H_2$
  - A: $Zn - 2e = Zn^{2+}$
  - Summary: $Zn + 2H^+ = Zn^{2+} + H_2$

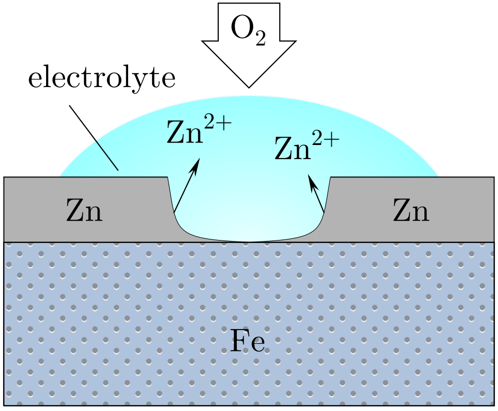
- Corrosion of zinc in neutral media without oxygen
  - C: $2H_2O + 2e = H_2 + 2OH^-$
  - A: $Zn - 2e = Zn^{2+}$
  - Summary: $Zn + 2H_2O = Zn(OH)_2\downarrow + H_2$

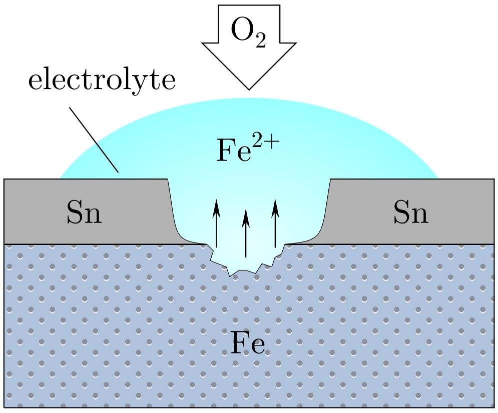
- The conclusion is that corrosion in neutral media occurs slowly due to insoluble corrosion products

3.4 Corrosion of contacting metals

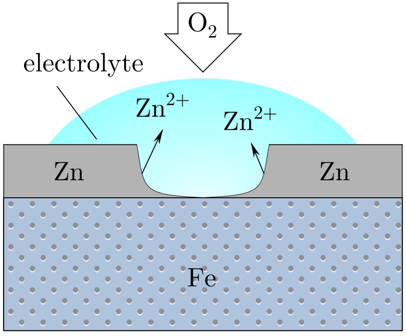
- Basic rules for the case of corrosion of metal in contact with other metals
  - A metal having a more negative standard potential (anode) will destroy
  - Another metal stays unchanged and plays a role of cathode on which oxidizer (H^+ or O_2) is reducted
  - The greater the difference in the standard potentials of the contacting metals the more intensive the corrosion is

- Corrosion pairs $\overset{-0.44}{\mathrm{Fe}}|\overset{-0.76}{\mathrm{Zn}}$ and $\overset{-0.44}{\mathrm{Fe}}|\overset{-0.14}{\mathrm{Sn}}$



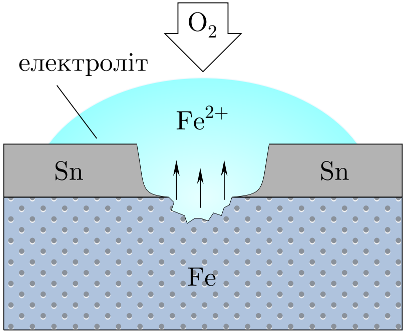


- Corrosion pair Fe|Zn (anodic coating)



$$E^\circ(Fe^{2+}/Fe) = -0.44\ V,$$
$$E^\circ(Zn^{2+}/Zn) = -0.76\ V$$
$$A: Zn - 2e = Zn^{2+}$$
$$C: O_2 + 2H_2O + 4e = 4OH^-$$

- Anodic coating protects a metal *even if damaged*
- Corrosion pair Fe|Sn (cathodic coating)



$$E^\circ(Fe^{2+}/Fe) = -0.44\ V,$$
$$E^\circ(Sn^{2+}/Sn) = -0.14\ V$$
$$A: Fe - 2e = Fe^{2+}$$
$$C: O_2 + 2H_2O + 4e = 4OH^-$$

- This coating protects a metal *until it is damaged*

3.5 The main factors that are influent on corrosion

Passivity of metal

- *Passivation is a process of appearing of protective film on metal surface*
- An example: $2Al + 2H_3PO_4 = 2AlPO_4\downarrow + 3H_2$
- Most often, the film is formed by oxide

  - $2Al + 3H_2SO_{4(dil)} = Al_2(SO_4)_3 + 3H_2$
  - $2Al + 3H_2SO_{4(conc)} = Al_2O_3\downarrow + 3SO_2 + 3H_2O$

- Depassivation is the reverse process. It is stimulated by **depassivators** which are certain anions:

$$SO_4^{2-}, OH^-, ClO_4^-, F^-, I^-, Br^-, Cl^-$$

- An example:
  - $Al + CuSO_4 \nrightarrow$
  - $2Al + 3CuCl_2 = 2AlCl_3 + 3Cu$

- Oxidizing anions (MnO_4^-, CrO_4^{2-}) can both accelerate corrosion (with reduction at the cathode) and slow it down (metal passivation)

pH influence

- A common rule: *the lower the pH*, the more the cathode potential, *so the more the corrosion rate*

- Metals are separated on five groups: metals that
  - having full corrosion resistance (Pt, Ag, Ti, Au)
  - are stable in alkaline solutions, but unstable in acidic ones (Cd)
  - are stable in acidic solutions, but unstable in alkaline ones (Ta, Mo, W)
  - are stable in neutral media only (Zn, Al, Sn)
  - are poorly stable in acidic medium, moderately stable in neutral one and passive in alkaline medium (Mg, Mn, Fe)

Influence of another factors

- The rate of corrosion is influenced by ions that
  - forms insoluble compounds on the metal surface (CO_3^{2-}, PO_4^{3-} on Fe)
  - are depassivators and rises the corrosion rate
  - hydrolyses and influences on pH

- Increasing the temperature speeds up corrosion. The exception is change in the reaction mechanism

$$Zn + 2H_2O \xrightarrow{90^\circ C} Zn(OH)_2\downarrow + H_2$$

Part II
Corrosion protection

4 Introduction

Corrosion protection: introduction

- Assessment of financial losses from corrosion
  - the developed countries: 2–4 % of Gross Domestic Product
  - USA: 3.1 % of GDP
  - metal losses – up to 20 % of annual steel production
- Basic methods of corrosion protection:
  - alloying
  - protective coatings
  - electrochemical protection
  - change in corrosive environment

5 Alloying

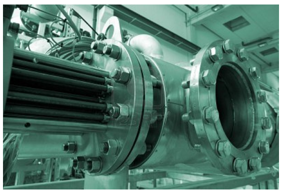
5.1 Description

Basics of Alloying

- Alloying means including of certain components to the steel composition. It causes the passivation of the base metal due to the formation of protective films on its surface
- These components are distributed evenly in all the metal volume, so
  - the corrosion resistance is maintained when scratching the surface
  - but alloyed steels are quite expensive
- Usage of alloyed steels

  - corrosion protection in gas media at higher T
  - protection of parts which are under intense mechanical stress




5.2 The materials

- Alloying not only protects from corrosion but improves the mechanical properties of the alloy
  - *heat-resistance* is the corrosion resistance at higher T
  - *high-temperature strength* is the mechanical strength at higher T
- Alloying elements and marking of steels
  Cr (Х), Ni (Н), Mn (Г), Si (С), Mo (М), W (В), Ti (Т), Ta (ТТ), Al (Ю), Nb (Б)
- For example: high-alloy steel 03Х16Н15М3Б
  - 03 is carbon content of 0.03 %
  - Х16 is 16% of chromium
  - Н15 is 15% of nickel
  - М3 is 3% of molibdenum
  - Б is up to 1% of niobium

6 The protective coatings

6.1 Paintwork

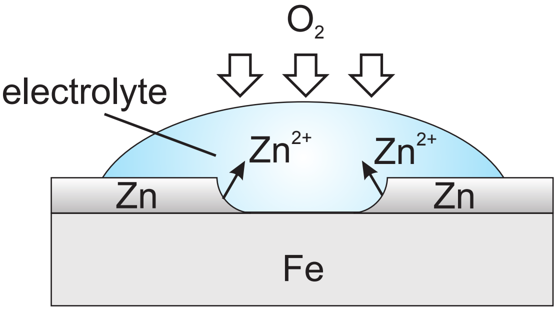
- The varnish is a mixture of resin and volatile solvent. Solvent evaporates with time and the resin becomes hard because of polymerization.
- Paint is a mixture of pigment with a binder. As a pigment can be used
  - metal oxides ($Fe_2O_3, TiO_2, ZnO, Cr_2O_3, Pb_3O_4$)
  - other inorganic compounds ($BaSO_4, PbSO_4, As_2S_3$)
- A principle is metal isolation from agressive medium

- Paintwork are
  - continuous
  - gas & water tight
  - chemically resistant
  - well retained on the surface

6.2 Metal coatings

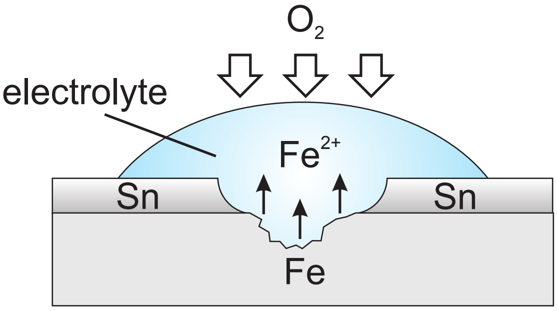
- Metal coatings are classified as *anodic* and *cathodic*

Anodic



$E^\circ(\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.44$ B,
$E^\circ(\mathrm{Zn}^{2+}/\mathrm{Zn}) = -0.76$ B
A: $\mathrm{Zn} - 2e = \mathrm{Zn}^{2+}$

Cathodic



$E^\circ(\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.44$ B,
$E^\circ(\mathrm{Sn}^{2+}/\mathrm{Sn}) = -0.14$ B
A: $\mathrm{Fe} - 2e = \mathrm{Fe}^{2+}$

$$\mathrm{C:}\ \mathrm{O_2} + 2\mathrm{H_2O} + 4e = 4\mathrm{OH}^-$$

- Cathodic coating protects the basic metal until coating is damaged
- Anodic coating protects the basic metal even when it damaged

6.2.1 Methods of applying metal coatings

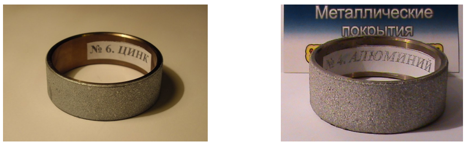
- *Sputter coating*
  - well retained on the surface
  - can be applied on parts having any form
  - can be of any metal, theoretically
  - the disadvantage is its porosity
- *Thermodiffusion*: when molten metal of coating penetrates into the basic metal
  - Zn and Sn coating can be applied on iron using this technique
  - coatings are of high quality

  - the disadvantage is that the melting point of coating metal should be lower than of basic metal

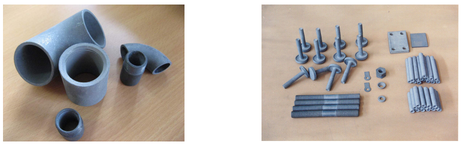
- *Plating*: hot rolling or drawing of base metal together with a metal of coating
  - the best quality of coating
  - the disadvantage is that it can be applied only on flat surfaces

Coatings applied in different ways

Sputtering



Thermodiffusion



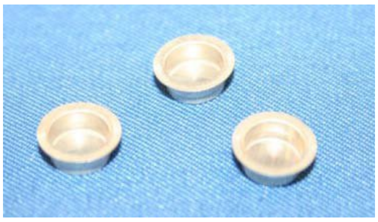
Plating

6.2.2 Coatings applied by oxidation of base metal

- *Oxidation* is applying of an oxide film
  - **bluing** is the oxidation of ferrous metals
  - **anodizing** is the oxidation of aluminium

- *Phosphating* is applying of a film consisting of phoshpate
  - is used for protection of ferrous metals
  - it is a good substrate for paintwork

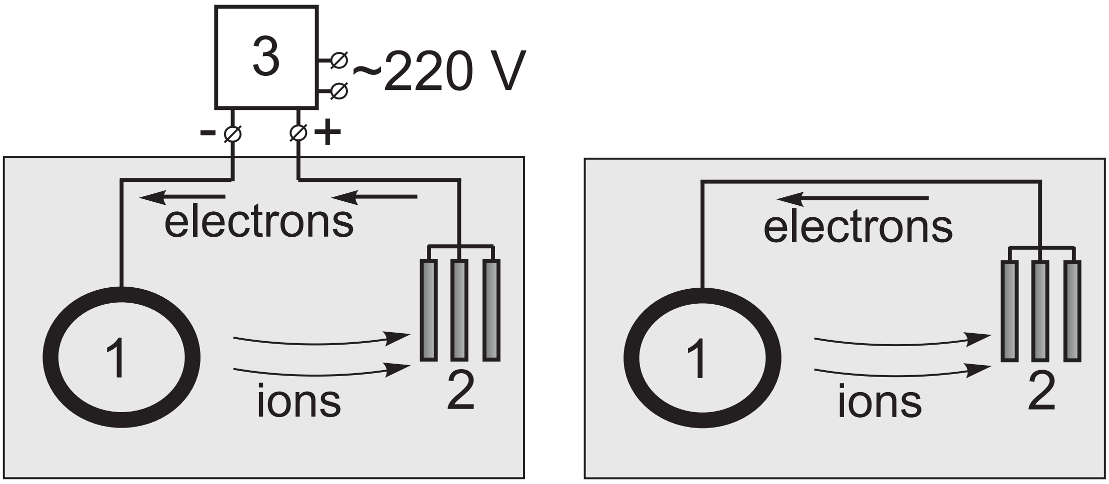
bluing



oxidation

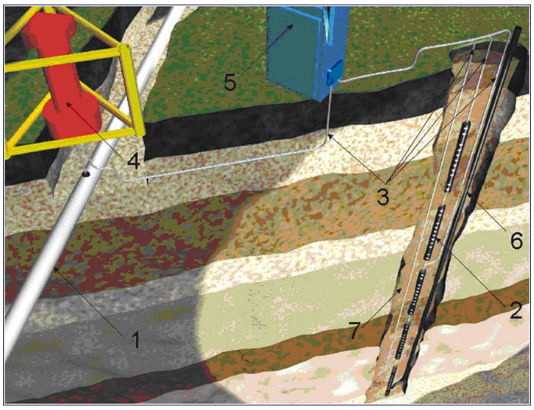
phosphating

6.3 Electrochemical protection

- can be used in conductive media (soil)
- A metal construction becomes *polarized*, i. e. its electrode potential changes due to
  - an external current source
  - a metal that has more negative potential
- 

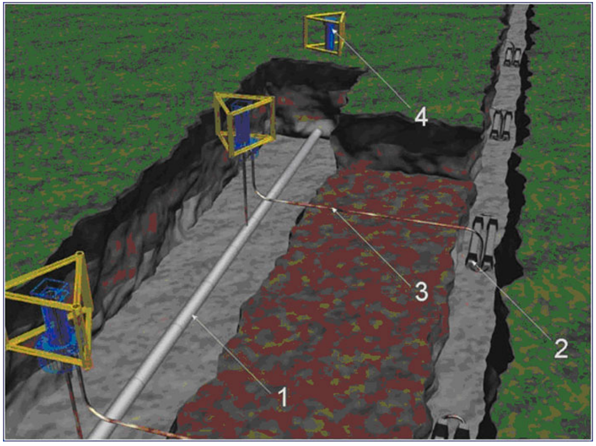
  1 – construction, 2 – anode, 3 – direct current source
  Cathode protection on the left picture, galvanic (sacrificial) protection on the right picture

Scheme of ICCP



1 – pipeline, 2 – anodic earthing electrode, 3 – connection cable, 4 – checkpoint, 5 – cathodic protection station, 6 – gas tubule, 7 – clay roses

Passive cathodic protection scheme



1 – pipeline, 2 – sacrificial anode, 3 – connection cable, 4 – checkpoint

7 Corrosion medium composition controlling

- It can be carried out in two ways
  - agressive components eliminating
  - corrosion inhibitors adding
- First way usually applied to heat equipment
- Oxygen elimination ways
  - heating
  - inert gas blowing (N_2)
  - chemical treatment (with iron sawdust or Na_2SO_3)

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

- pH controlling is important for processes accompanied by hydrogen depolarisation ($E(2H^+/H_2) = -0.059\text{pH}$)

7.1 Corrosion inhibitors

- A corrosion *inhibitor* is a chemical compound that decreases the corrosion rate

- They are effective for isolated systems (heating&cooling pipelines)

- By action mechanism, inhibitors can be *anodic*, *cathodic* and mixed

- By medium: inhibitors, that active in acidic, alcaline or neutral media

- Protective layers formed by corrosion inhibitors are always thinner that any coatings

Anodic inhibitors

- They decrease anode area but don't affect a corrosion mechanism:
  - passivators grow an oxide film
  - film-forming inhibitors create an adsorbed layer

- Passivators are:
  - *safe inhibitors* ($CrO_4^{2-}, NO_3^-, NO_2^-$) act only on anode
  - *unsafe inhibitors* (H_2O_2) can be more active but they accelerate cathodic process

- Film-forming inhibitors:
  - phosphates and polyphosphates
  - $NaOH$ and Na_2CO_3
  - organic surfactants

Cathodic inhibitors

- Cathodic inhibitors:
  - they modify a corrosion mechanism

$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

- decrease cathode area ($Ca(HCO_3)_2$)
  K: $O_2 + 2H_2O + 4e = 4OH^-$,
  $Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O$
- organic inhibitors adsorb on cathode and decrease its area