Abstract

This seminar presents the problem of corrosion of metals and alloys. An introduction is made about the types of corrosion, the damage it causes and the significance of recognition of the corrosion mechanisms. We describe the thermodynamics and kinetics of corrosion process.
1. Introduction

Corrosion is a destructive attack on the metal by its reaction with the environment. It is based on chemical and electrochemical reactions that occur due to thermodynamic instabilities in the environment. [1] Some typical corrosive environments are air and humidity, water (fresh, distilled, salt), atmospheres (natural, urban, marine, industrial), steam and gases. Like metals, other materials (such as plastic, ceramics,...) also undergo degradation, but the term 'corrosion' refers (usually) only to metals. Metals have some technically important properties like tensile strength, temperature resistance, electrical and thermal conductivity, etc., which differ them from other materials. Normally all crucial components of machines, cars, instruments are made of metal. Therefore the durability of all of them is dependent on their corrosion resistance. But a big problem with corrosion is that we do not realize it happening until some damage is already done, mostly in industry (loss of efficiency, product, money due to repairs), storage (leaking, contamination), transport, construction (buildings, bridges - steel reinforcements in concrete). Because of the scale of the damage, the cost associated with corrosion is extremely high. For most industrialized nations, the average corrosion cost is between 3,5 and 4,5 % GNP. [1] The costs and damage can be lowered by using adequate preventive measurements. With the right choice of materials and surface treatment, the rate of corrosion can be kept sufficiently small.

2. Generally about corrosion

The majority of metals in nature appear in the form of sulphides and oxides. A lot of energy is required to get them into the form of a pure metal. That means they are thermodynamically unstable
in nature and the process of transforming back into their original form is spontaneous. Corrosion of metals is therefore inevitable.

The process of corrosion can be described as a galvanic cell. A scheme is represented in Figure 1a. The cell represents a closed electric circle, consisting of two metal electrodes in an aqueous solution: anode and cathode. If the electrodes are linked by a conductor, there will be a current flowing from the cathode to anode because of the difference in potential - nobility. The nobility is determined by electropotential series which includes all metals and semi metals, placed in order by the value of their potential. Noble metals are those that are resistant to oxidation (for instance Au, Ag, Pt). On the anode occurs oxidation – loss of material (1) and on the cathode occurs reduction (2)-(5). The reduction reactions can be different when the metal is exposed to different environments. The most common reactions are: (2) formation of hydrogen, (3) reduction of oxygen in an acidic environment, (4) reduction of oxygen in an alkaline environment and (5) reduction of a metal ion. [4] Writing the reactions:

\[ M \rightarrow M^{n+} + ne^- \]  \hspace{1cm} (1)

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (2)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm} (3)

\[ O_2 + 2H_2O + 4e^- \rightarrow 5OH^- \]  \hspace{1cm} (4)

\[ M^{n+} + ne^- \rightarrow M^{(n-1)+} \]  \hspace{1cm} (5)

A process like this does not always involve two different metals. Both partial reactions (oxidation and reduction) can also appear on the same metal. Usually a metal surface is not entirely homogenous (on the microscopic level). There can be defects such as edges, kink sites, steps or surface contaminants like the presence of an impurity metal atom or adsorption of ions from solution. [2] Some of these defects are presented in Figure 1b. Consequently there are small differences in local potential. When the metal comes into contact with the electrolyte the differences in potential cause the redox reactions to occur in a coupled manner. Microgalvanic cells are formed on the surface of the metal – cathodic and anodic sites, that start the corrosion.

![Figure 1: A scheme of a galvanic cell (a) and the heterogeneous nature of a metal surface (b).](image) [2]
The mass of corroded metal can be calculated from Faraday’s law. According to this law, an electric charge $Q$ passes across the electrode-electrolyte interface when $n_i$ moles of a given substance react [1]:

$$ Q = n \cdot F \cdot n_i $$  \hspace{1cm} (6)

$F$ designates the Faraday constant: $F = 96,485 \text{ C/mol}$ and $n$ represents the charge number (dimensionless), which indicates the number of electrons exchanged in the dissolution reaction. The amount of substance is defined as $n_i = m_i / M_i$, where $m_i$ is the mass of the substance and $M_i$ is the molar mass. The derivative of the equation (3) with respect to time gives the form of Faraday’s law that is most often in use.

$$ I = nF \frac{dn_i}{dt} $$  \hspace{1cm} (7)

Here $I$ is the current $I = dQ/dt$ and $dn_i/dt$ represents the rate of reaction in moles per second.

### 2.1 Types of corrosion

There are two major types of corrosion: uniform and localized corrosion. Uniform corrosion represents evenly attacked metal over its entire surface. The cathodic and anodic sites are formed on the surface, as mentioned above, but their position changes with time. The overall effect is that the metal is uniformly attacked, so the thickness of the metal is evenly decreasing. This type of corrosion is well recognizable, easier to monitor and could be solved by adequate protection of the metal.

![Figure 2: Schematic representation of uniform corrosion and three types of localized corrosion – pitting, crevice and stress corrosion cracking.][2]
Localized corrosion takes place when the corrosion progression is not uniform. In this case the cathodic and anodic sites do not change their position, they are fixed. The corrosion proceeds on established portions of the metal surface. There are more types of localized corrosion. The most common forms are: pitting corrosion, crevice corrosion and stress corrosion cracking. [2] With pitting corrosion, the area where corrosion occurs is very small, the pits are much deeper than their diameter. This type of corrosion is very difficult to predict and monitor and it causes a lot of damage. Crevice corrosion occurs at cracks, filled with corrosion medium, usually at junctions or threads. The oxygen level in the crevice is very poor, while on the surface it is much higher. Therefore the surface takes the role of the cathode and in the crevice anodic reaction occurs – dissolving the metal. If the material is under mechanical stress and exposed to corrosive medium the stress corrosion cracking occurs. The result is reduced tensile strength of the material. Shematic representation of the types of corrosion is in Figure 2.

3. Thermodynamics of corrosion reactions

To understand and to quantify the corrosion phenomena the study of chemical and electrochemical equilibrium is required. Most corrosion reactions occur at constant temperature \( T \) and pressure \( p \). Therefore the most convenient state function for describing equilibrium is Gibbs free energy, also known as free enthalpy \( G = H - TS \). Here the symbols \( H \), \( T \) and \( S \) represent enthalpy, temperature and entropy, respectively. Total derivative of Gibbs free energy is:

\[
dG = -SdT + Vdp \tag{8}
\]

Equation (5) applies to a closed system. If the system contains \( n_i \) moles of various species \( i \), then (5) can be extended to:

\[
dG = -SdT + Vdp + \sum \mu_i dn_i \tag{9}
\]

Where \( \mu_i \) is chemical potential which, in pure substance, is equal to the molar free energy. It is defined as

\[
\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \tag{10}
\]

A chemical reaction can be expressed in the following way

\[
0 = \sum v_i B_i \tag{11}
\]

Here the \( v_i \) are the stichiometric coefficients. For the products of the reaction they are positive and for the reactants they are negative. The participant species in the reaction are represented by \( B_i \). The change in Gibbs free energy can be written as
\[ \Delta G = \sum v_i \mu_i \]  

By integrating equation (5) and using the definition of the chemical potential we get the alternate definition for ideal solution

\[ \mu_i = \mu_i^0 + RT \ln a_i . \] (13)

Here \( \mu_i^0 \) represents the standard chemical potential and \( a_i \) is the activity of the \( i \)th species. By convention \( a = 1 \) for liquid H\(_2\)O and solids. For other liquids and for ions the activity \( a \) is replaced by concentration \( c \) and for gases activity \( a \) is replaced by pressure \( p \).

In chemical equilibrium the Gibbs free energy has its minimum \( \Delta G = 0 \). If the free energy is negative \( \Delta G < 0 \), the corrosion reaction is spontaneous. Introducing (13) into (12) and defining equilibrium constant \( \ln K = \sum v_i \ln a_i \), we get:

\[ \Delta G = \Delta G^0 + RT \ln K \] (14)

The electrochemical cell can supply electrical work due to the transport of electrons via the conductor that links the two electrodes. The maximum work that a cell can provide, can be calculated from the equation (15). The free energy of the redox reaction is equal to the supplied work:

\[ \Delta G = W_e = -nFE_{rev} \] (15)

\( E_{rev} \) is the reversible potential or equilibrium potential of the cell reaction. It is defined as the difference in electric potential between the metal and the solution at equilibrium. [1] Under standard conditions the equation (12) is \( \Delta G^0 = -nFE^0 \), where \( E^0 \) is the standard potential of the cell reaction.

### 3.1 Nernst equation

Nernst equation allows the calculation of the equilibrium potential as a function of concentration (activity) and temperature. It applies to electrodes at equilibrium. [1] An electrochemical cell includes two half-cell reactions - oxidation and reduction. The equation of the cell can be written as:

\[ \sum v_{ox,i} B_{ox,i} + ne = \sum v_{red,i} B_{red,i}. \] (16)

The left side of the equation describes the process of oxidation and he right the process of reduction; \( v_{ox,i} \) and \( v_{red,i} \) represent the stoichiometric coefficients and \( B_{ox,i} \) and \( B_{red,i} \) are the 'oxidized' and 'reduced' species. For comparison of equilibrium potentials of different electrode reactions a convention was needed to scale the standard electrode potentials. A value of zero was assigned to the equilibrium potential of hydrogen electrode kept at standard conditions - \( pH = 0 \) (\( P_{H_2} = 1 \) bar, \( T=298 \) K, \( a_{H_2}=1 \)). [1] The equation (16) becomes:
\[
\sum v_{\text{ox},i} B_{\text{ox},i} + \frac{n}{2} H_2 = \sum v_{\text{red},i} B_{\text{red},i} + nH^+ \tag{17}
\]
and has its free energy [1]:

\[
\Delta G = \Delta G^0 + RT \ln \left( \frac{a_{\text{H}^+}^{\text{n}} \prod a_{\text{red},i}^{v_{\text{red},i}}}{p_H^{n/2} \prod a_{\text{ox},i}^{v_{\text{ox},i}}} \right) \tag{18}
\]

The symbols \(a_{\text{red},i}\) and \(a_{\text{ox},i}\) are the 'oxidized' and 'reduced' activities. Considering equation (15) and the values \(P_H=1\) bar and \(a_{\text{H}^+}=1\), the equation (18) becomes the general form of Nernst equation for any electrochemical system:

\[
E_{\text{rev}} = E^0 + \frac{RT}{nF} \ln \left( \frac{a_{\text{red},i}^{v_{\text{red},i}}}{a_{\text{ox},i}^{v_{\text{ox},i}}} \right) \tag{19}
\]

The standard potentials of electrode reactions \(E^0\) were numerically given as an electrochemical series, from which we can estimate the resistance to corrosion for different metals. However, the series takes into account only very pure metals at idealized conditions. The realistic corrosion systems are much more complex for Nernst equation to predict exact thermodynamic behaviour. Usually the system is not in equilibrium which is the condition for reversibility. Despite this effect, the Nernst equation is universal enough to be used for assessing the thermodynamic stability of a system.

The corrosion thermodynamic information for a given metal can be summarized in potential-pH diagrams. They are called Pourbaix diagrams and they represent Nernst equation as a function of pH. For a given metal, the diagram is drawn by taking into account of all possible reactions at 25°C. Electrochemical equilibrium between a metal and its ions, a metal and its oxide, two oxides of different oxidation states and chemical equilibrium in acidic solution between an oxide and dissolved ions, basic solution between an oxide and dissolved ions. [1] The symbol \(M\) indicates the metal and \(O\) the oxidising agent.

A stable phase of species can be determined from these diagrams as they represent the stability of a metal as a function of potential and pH at particular combinations of these two quantities. A diagram is constructed by calculations based on Nernst equation and solubility data for a metal and its species in equilibrium. It indicates regions of stability such as regions of passivity, immunity and corrosion of a metal. With Pourbaix diagram we can determine the corrosion behaviour of a metal by knowing the potential dependance of the three states of a metal in a corrosive medium; active state (corrosion), thermodynamic stability (immunity of a metal) and a phase of forming a passive layer which inhibits the corrosion process on the metal surface (passivity of a metal). The Pourbaix diagram for aluminium is shown in Figure 4c. [2]
The diagram shows three types of lines. Horizontal lines are for reactions involving only the electrode potential $E$ and they represent electron transfer reactions. Vertical lines are for reactions that are pH-dependent and not accompanied by any electron transfer. The slanted lines pertain to reactions that involve both the electrode potential $E$ as well as pH. These lines show the equilibrium conditions, that is, where the activities are equal, for the species on each side of that line. On either side of the line, one form of the species will instead be said to be predominant. [6] Another type of dashed, slanted lines represents the stability region of water (between a and b) at ambient pressure. The region above the b line (high $E$/pH) is highly oxidising, leading to oxidation of $H_2O$ to $O_2$. In contrast, the highly reducing conditions (low $E$/pH) below the a line lead to reduction of $H_2O$ to $H_2$.

## 4 Kinetics of corrosion

### 4.1 Charge transfer – single electrode

When a piece of metal is submerged in an electrolyte a charge separation occurs at the electrode-electrolyte interface. The transfer of the electrons is not unobstructed anymore because of the established electric field ($10^8$ to $10^9$ V/m). The spatial region is called the electric double layer and is about a few nanometers thick. A scheme of the reactions that occur during corrosion in the solution is represented in Figure 4(a,b). Let us consider the transfer of $n$ electrons between the two species, $B_{ox}$ and $B_{red}$.

$$B_{red} \rightleftharpoons B_{ox} + ne \quad (20)$$

The current density across the interface is proportional to the rate of the reaction, according to Faraday’s law (7). Because the reaction can take place in both directions, its rate is the difference of cathodic $\nu_c$ and anodic rate $\nu_a$, multiplied by $nF$, $i = nF(\nu_a - \nu_c)$. The current can be rewritten as:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left( \frac{D}{\eta} \frac{\partial \rho}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{D}{\eta} \frac{\partial \rho}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{D}{\eta} \frac{\partial \rho}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{D}{\eta} \frac{\partial \rho}{\partial z} \right)$$
\[ i = k'_{a(E)}c_{\text{red},s} - k'_{c(E)}c_{\text{ox},s} \]  \hspace{1cm} (21)

Where are \( k'_{a(E)} \) and \( k'_{c(E)} \) the potential-dependent rate constants and \( c_{\text{red}}, c_{\text{red}} \) represent the surface concentrations of reduced and oxidized species at the electrode surface respectively. The rate constants obey Arrhenius’ law:

\[ k'_{i(E)} = k'_{i,0} \exp\left(-\frac{\Delta G^\#}{RT}\right) \]  \hspace{1cm} (22)

\( \Delta G^\# \) represents the activation energy of a partial reaction, and \( k'_{i,0} \) are pre-exponential factors. The activation energies are modified by the presence of an electric field at the electrode \( \Delta \phi \), as seen schematically in Figure 5.

\[ \Delta G^\#_a = \Delta G^\#_{a,\text{ch}} - \alpha F \Delta \phi \]  \hspace{1cm} (23)

\[ \Delta G^\#_c = \Delta G^\#_{c,\text{ch}} + (1 - \alpha) F \Delta \phi \]  \hspace{1cm} (24)

The factor \( \alpha \) is the charge transfer coefficient and it describes the fraction of the effect of the applied electric field on the activation energy for the partial reactions that occur on the surface of that electrode. For a positive potential applied, the electric field diminishes the activation energy of the anodic partial reaction and increases that of the cathodic partial reaction (Figure 5). [1] Meaning that probability for oxidation is higher with its threshold of activation energy being lowered. On the opposite, for a reverse reaction the threshold of activation energy increases. Under the assumption that \( \Delta G^\#_i \) varies linearly with \( \Delta \phi \), the charge transfer coefficient is a constant with its value between

![Figure 5: Influence of the potential on the activation energy for charge transfer at electrode-electrolyte interface.](image-url)
0 and 1. [1] The value is normally around 0.5, resulting in a curve’s maximum being located at the mid-point between initial and final state.

The value of $\Delta \phi$ differs by a constant from the potential of the electrode $E$, which is measured with respect to the standard hydrogen reference electrode. Therefore $E$ can be written as $E = \Delta \phi + \text{constant}$. Introducing equations (20) and (21) into (19), the potential independent terms can be grouped together in constants $k_a$ and $k_c$. The equation (18) can be rewritten as:

$$i = nFk_ac_{\text{red},s} \exp\left(\frac{\alpha nF}{RT}E\right) - nFk_cc_{\text{ox},s} \exp\left(-\frac{(1 - \alpha)nF}{RT}E\right)$$

(25)

Here the current $i$ corresponds to the sum of partial anodic and cathodic current densities $i = i_a + i_c$.

At equilibrium, $E = E_{\text{rev}}$, the net current density is zero ($i = 0$) and the concentrations of species on the surface of the electrode are equal to those in the bulk solution, $c_{\text{red},s} = c_{\text{red},b}$ and $c_{\text{ox},s} = c_{\text{ox},b}$. The exchange current density can be defined as:

$$i_0 = i_a(E_{\text{rev}}) = -i_c(E_{\text{rev}})$$

(26)

Introducing (20) into (19) yields:

$$i = i_0 \exp\left(\frac{\alpha nF}{RT} \eta\right) - i_0 \exp\left(-\frac{(1 - \alpha)nF}{RT} \eta\right)$$

(27)

here the overvoltage $\eta = E - E_{\text{rev}}$ was introduced. The concentrations of the species were assumed to be homogenous in the electrolyte. Equation (27) is the usual form of Butler-Volmer equation. It describes the relationship between current density and potential for a simple electrode reaction, controlled by charge transfer [3]. The precise course of the reactions in a corroding system is often unknown. As it turns out, it is quite useful to introduce the empirical Tafel coefficients $\beta_a$ and $\beta_c$.

$$\beta_a = \frac{dE}{d\ln i_a} = \frac{RT}{\alpha nF}$$

(28)

$$\beta_c = \frac{dE}{d\ln |i_c|} = \frac{RT}{(1 - \alpha)nF}$$

(29)

We get the Butler-Volmer equation in the form of:

$$i = i_0 \exp\left(\frac{\eta}{\beta_a}\right) - i_0 \exp\left(-\frac{\eta}{\beta_c}\right)$$

(30)

Figure 6.a represents the current density as a function of potential (30) on a linear scale. The current density at equilibrium is zero. In order to determine the quantities $i_0$, $\beta_a$, $\beta_c$ experimentally, the
current is also shown on a logarithmic scale. This type of curve is called the Tafel curve. It is the basic yet very efficient way to determine the kinetic parameters of a corroding system.

Figure 6: Partial current densities and total current density near the equilibrium potential (a), and the Tafel curve (b). [1]

The slope has two regions: anodic and cathodic Tafel region. The parameters can be determined from the linear section of the region, as shown in Figure 6.b. When the potential corresponds to $\eta/\beta_a \gg 1$, the region is anodic. The current density can be expressed:

$$i = i_a = i_0 \exp \left( \frac{\eta}{\beta_a} \right)$$

(31)

For the cathodic region the potential corresponds to $\eta/\beta_c \ll -1$. The cathodic current density is:

$$i = i_c = i_0 \exp \left( -\frac{\eta}{\beta_c} \right)$$

(32)

4.2 Charge transfer – mixed electrode

So far the kinetics of a single electrode has been discussed. The model involves one partial reaction taking place on a metal surface at a specific time. But, for example, if we are dealing with uniform corrosion, both redox reactions can occur simultaneously. The system is called a mixed electrode. Let us write a reaction where a metal M dissolves while a species $B_{ox}$ is reduced to $B_{red}$.

$$M + v_{ox}B_{ox} \rightarrow M^{n+} + v_{red}B_{red}$$

(33)

The total current density equals to the contributions of anodic and cathodic partial current densities of the electrode reactions:

$$i = i_M + i_B = i_{a,M} + i_{c,M} + i_{a,B} + i_{c,B}$$

(34)

The equation can be simplified by the fact that in the corroding system, the values of $i_{c,M}$ and $i_{a,B}$ are very close to zero. The equilibrium potential in a mixed electrode system is called the corrosion potential $E_{cor}$. When $E = E_{cor}$ there is no net current ($i = 0$) and the corrosion current density can be defined as:

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\[ i_0 = i_{a,M(E_{cor})} = -i_{c,B(E_{cor})} \]  

(35)

The Butler-Volmer equation describes each partial reaction if charge transfer rate is limited. [1] By defining the polarization as \( \zeta = E - E_{cor} \), the Butler-Volmer equation for mixed electrode system can be expressed [1] in the same form as equation (27):

\[ i = i_{cor} \exp\left(\frac{\zeta}{\beta_{a,M}}\right) - i_{cor} \exp\left(-\frac{\zeta}{\beta_{c,B}}\right) \]  

(36)

6 Conclusion

Corrosion represents severe problems in many areas, such as transport, industry, construction, etc because of the wide use of metals. In an aggressive environment, metals are exposed to severe degradation. Therefore the need for corrosion monitoring and control are extremely high. Corrosion is an electrochemical process, depending on the thermodynamics and kinetics of a chemical reaction. Corrosion process differs for different metals also depending on the environment the metal is in, meaning different types of corrosion, rates, products, mechanisms, etc. By developing the adequate methods, which allow the insight into the mechanisms of corrosion process, a lot of progress has been done in the corrosion control.

References


