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Metal corrosion and its relation to other fields of science

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Abstract

Metal corrosion is a charge transfer process. Study of corrosion and corrosion protection requires manifold knowledge in the field of thermodynamics, reaction kinetics, catalysis, transport and surface phenomena. Dealloying, biocorrosion, corrosion effects of electric traction and energy systems are also very important scientific fields for understanding corrosion.

Key words: *metal corrosion, charge transfer, catalysis in corrosion, bimetallic and multimetallic corrosion, adsorption, inhibitors, biocorrosion.*

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Study and knowledge of metal corrosion and corrosion protection is a very important field of modern research and development, because everybody experiences metal corrosion who use appliances made of metals. The man met with metal corrosion at the dawn of human civilization, but the methods of corrosion protection have been developed very slowly, mostly experientially [1–4].

The methods developed experientially, step by step became scientifically grounded technologies, in fact, certain technologies were developed on the basis of scientific-technological development (for instance, cathodic protection or electroplating, etc.). The scientific development of bases of corrosion protection technologies is still going on, and for this reason, these methods become simpler and more effective.

The technologies used in the industry never rely on the results of only one scientific field, but apply more or less the results of every scientific field by which the technical level of a given technology can be increased [2, 3]. This is also true for metal corrosion, also.

The scientific, technical and common language name the process metal corrosion, the result of which at first the surface, later the bulk of the metals, in a result of spontaneous reactions with materials of the environment, undergo chemical changes, therefore, the metal corrosion is a chemical, moreover a charge transfer chemical process (which is very often called anodic process), consequently, the main point of metal corrosion is the losing electrons of metals:

$$Me \leftrightarrow Me^{z+} + ze \qquad (1)$$

where Me^{z+} can be any product of metal corrosion, ‘z’ is charge transfer number. Losing electrons can take place in wet environment, or in gas phase for we talk about only

oxidation. Several similarities can be experienced between the metal corrosion taking place by the two ways because the effect of water cannot be closed out even in dry environment [1].

According to Marcus also, metal corrosion in wet environment is an electrochemical process [1]. If in a wet system characterised by process (1) there is no electron-consuming process, the system reaches an equilibrium, and the measurable electrode potential is an equilibrium potential (in this case no corrosion). If there is an electron-consuming process in the system (the so called cathodic process), then equilibrium (1) is shifted to the right, and metal corrosion takes place. In this case the measurable electrode potential is not an equilibrium potential but a mixed (a corrosion) potential. It follows from the earlier considerations that knowledge of physicochemical characteristics of charge transfer chemical processes may help a lot to understand the reasons of metal corrosion.
It is well known, that in the course of the corrosion process (1), energetic changes take place, for this, the scientific knowledge of the energetic (thermal) processes of metal corrosion are of basic questions in this field [1–9].

1. The thermodynamic bases of metal corrosion

At the very beginning of scientific cognition of chemical processes it was imagined that chemical processes take place when the reacting system lose energy, *i.e.*, the system warms. This idea was supported, for instance, by the knowledge of fire, the dilution of sulphuric acid, burning oil or grease, the gunpowder, etc. It follows from the above statement that the enthalpy (H) change: $-\Delta H$, that is a negative number, because the reacting system loses energy [1, 5, 6].

The idea about heat energy change of chemical processes seemed true for great many of chemical reactions, but there were exceptions. Such processes take place also spontaneously which absorb heat from their environment, therefore, $+\Delta H$, that is, the system cools down. Explanation of this phenomenon was given by the development of thermodynamics. It was the understanding of the role of entropy ($\mathrm{d}q = T\mathrm{d}s$) in chemical processes, creating of Gibbs energy function ($g = h - Ts$) and introduction the concept of chemical potential ($\mu = \mu^{o} + RT \ln a$).

It turned out, that chemical processes take place not in the direction of enthalpy (H) decrease, but in the direction of Gibbs energy (G) decrease, therefore, the driving force of chemical processes is $-\Delta G$ (capital G and H mean molar values). In the case of processes, where the entropy change is large but the enthalpy change is small, that is, $\Delta H < T\Delta S$, the process takes place with heat absorption, therefore, it is endothermic, consequently, the system cools down.

The thermodynamic state of metals changes as a result of industrial metal processing, for instance, welding, heating, hammering, bending, *etc*. Unfortunately, this is very often ignored in discussions of reasons of metal corrosion.

2. Energy changes of charge transfer chemical processes

For the most part of chemical processes, energy changes mostly thermal energy changes can be observed. In the case of charge transfer chemical processes, however, the change of electric energy also takes place in the process. It was understood, when Me metal is in the solution of Me^{z+} ions (reaction (1), reaches an equilibrium, then:

$$\Delta G = -zFE \tag{2}$$

therefore, electric (zFE) and thermal (ΔG) energy change is equal with each other, for this reason, the system seems to be unchanged (F is the Faraday number and E is the electrode potential of Me metal).

The species taking part in process (1) have activities (a_{Me} and a_{Me}^{z+}), and chemical potentials (μ_{Me} and μ_{Me}^{z+}). Considering, that in this case $\Delta\mu = \Delta G$, and using equation (2) a relationship between activities (concentrations) and the equilibrium electrode potential (E) can be obtained:

$$E = E^0 + \frac{RT}{zF} \ln \frac{a_{Me^{z+}}}{a_{Me}} \tag{3}$$

what was recognized by W. Nernst, therefore, it is called Nernst equation. In equation (3), E is equilibrium electrode potential, E^0 its standard value, R is the gas constant and T is the absolute temperature. The equation is widely used to describe equilibrium conditions also in the field of metal corrosion [1, 6–9].

Monographs dealing with theoretical questions deal mostly with pure metals in equilibrium at 25°C, when $a_{Me} = 1$. In industrial production it is rarely the case, because heat treatment, welding, hammering, bending and other technological processes increase the metal activity, therefore, $a_{Me} > 1$, what should be taken into consideration.

The most important result of studies on equilibrium charge transfer chemical processes of metals is the so called Pourbaix diagrams, which describe graphically the thermodynamic properties of metals as a function of pH and electrode potential (E), at 25°C and 10^5 Pa (or one atmosphere) [9].

Here must also be mentioned the thermodynamic immunity, which has basic importance in understanding of cathodic protection [9]. A metal is in the state of thermodynamic immunity, if it is in equilibrium with its environment, or its equilibrium potential is much more negative than its standard electrode potential: $E << E^0$. The cathodic protection for iron works at a potential about 0.09 V more negative (at about –0.534 V) than the standard potential of iron ($E^0_{Fe^{2+}/Fe} = -0.440$ V) (potentials with respect to SHE (standard hydrogen electrode). –0.534 V with respect to copper/copper-sulphate electrode is –0.850 V, which means that iron at this potential is in equilibrium with 10^{-3} M solution of Fe^{2+} ion. In industrial practice iron is considered to be in thermodynamic immunity at this potential [10, 11]. (The –0.850 V working potential is NACE standard.)

2.1. Reference electrodes

One of the most important results of electrochemical thermodynamics is the developments of electrodes with constant electrode potential. These electrodes are the reference electrodes. Their common characteristics is their potential determining equilibria is in accordance with theoretical considerations. Reference electrodes have always been equilibrium systems. Their electrode potential can be calculated with the Nernst equation (3). There are two kinds of reference electrodes, the first and the second kind electrodes.
A well known reference electrode of the first kind is the hydrogen electrode which is rarely used in industrial practice, but its knowledge is still very important because it is the most important reference electrode (the 0 point of redox potential tables is the potential of SHE (standard hydrogen electrode)). Another reason of its importance is connected with corrosion reaction mechanisms because hydrogen deposition is one of the most important cathodic process in metal corrosion.

The potential-determining equilibrium of the hydrogen electrode:

$$H^+ + e \leftrightarrow ½\ H_2 \tag{4}$$

which is a catalytic process, for this reason platinized platinum (a catalyst) is the electrode material [12].

The copper/copper-sulphate electrode used in cathodic protection is also an electrode of first kind [12], where the potential-determining equilibrium is:

$$Cu \leftrightarrow Cu^{2+} + 2e \tag{5}$$

Electrode potential of this electrode is 0.316 V with respect to SHE.

A widely used electrode of the second kind is the calomel electrode [12]. The potential-determining equilibrium of this electrode:

$$Hg_2^{2+} + 2e \leftrightarrow 2Hg \text{ and } Hg_2Cl_2 \leftrightarrow Hg_2^{2+} + 2Cl^- \tag{6}$$

where the activity of Hg_2^{2+}, consequently, the potential of this electrode can be changed by adding KCl salt to the electrolyte, because Hg_2Cl_2 is poorly soluble in water [12]. The potential of saturated calomel electrode is 0.241 V (saturated means the electrolyte is saturated with KCl).

In industrial practice the hydrogen and the $Cu/CuSO_4$ electrodes are the electrodes of the first kind. The calomel and the silver/silver chloride electrodes are the most frequently used electrodes of the second kind [12].

3. Rate of charge transfer processes

After understanding of the equilibrium conditions in metal corrosion, the next question to be solved is the knowledge of reaction rate of processes. Naturally, in the case of chemical equilibrium macroscopic chemical reaction, consequently, metal corrosion cannot take place. The condition of a corrosion process is the existence of nonequilibrium conditions, which are of fundamentals for metal corrosion.

In the field of electrochemistry, consequently, is the field of metal corrosion also, the deviation from equilibrium conditions is called overvoltage (η), which is ($\eta = E_{pol} - E$), where E_{pol} is electrode potential and E is equilibrium potential. The relationship between reaction rate ($i = I/A$, where i is current density, I is current, and A is surface area) and overvoltage (η) was recognized by Erdey–Grúz and Volmer [1, 6, 8, 13]:

$$i = i^0 \left\{ \exp\left[\frac{\alpha z F}{RT} \eta \right] - \exp\left[\frac{-(1-\alpha) z F}{RT} \right] \eta \right\} \tag{7}$$

where i^0 is exchange current density, α is the charge transfer coefficient, 'z' is the charge transfer number.

The equation number (7) can be applied to describe any kind of charge transfer reaction, consequently, it is applicable to calculate metal corrosion reaction rate, if the rate determining step is the charge transfer reaction itself. Evans diagrams used to determine corrosion reaction rate are based on equation (7).

4. The rate of metal corrosion

The metal corrosion takes place without outer electric polarization, therefore electrons liberated in this process must be consumed in another chemical process, consequently, an electron-sinking process must be connected to a corrosion process (1), that is, a cathodic process, for instance:

$$\mathrm{Ox} + n\mathrm{e} \leftrightarrow \mathrm{Red.} \tag{8}$$

Simultaneous happening of processes (1) and (8) is the basic condition of metal corrosion. There is no corrosion if reaction (8) is hindered. Naturally, in the course of metal corrosion there are several anodic and cathodic chemical processes, therefore the corrosion reaction rate (I_{cor}) is:

$$I_{cor} = \Sigma I_a = \left| -\Sigma I_c \right| \text{ or } \Sigma I_a + \Sigma I_c = 0, \tag{9}$$

where I_a is the rate of anodic and I_c the rate of cathodic processes.

On the basis of relationships (1), (7), (8) and (9) the rate equation of a metal corrosion process, supposing the existence of only one cathodic and an anodic process:

$$I_{cor} = I_{Me}^0 \exp\left[\frac{\alpha z F}{RT} \eta_{Me} \right] = I_{ox}^0 \exp\left[\frac{-(1-\alpha) n F}{RT} \eta_{ox} \right] \tag{10}$$

if the reverse reactions are ignorable. The overvoltages are: $\eta_{Me} = E_{cor} - E_{Me}$ and $\eta_{ox} = E_{cor} - E_{ox}$; I^0 are exchange currents and E_{cor} is the potential of the corroding metal.

The corrosion potential (E_{cor}) is a mixed potential, therefore, it is a reaction kinetic and not a thermodynamic, that is, not an equilibrium quantity. It is the Wagner–Traud mixed potential, and it can be applied when the rate determining step is the charge transfer reaction [1, 14]. Finally, it have to be remarked that in the practice several units of reaction

rate are used in metal corrosion. The theoretical relationships are applicable in the case of any unit, but it must be taken into consideration the in one calculation only one unit can be used.

The metal corrosion is a multi step process, where not only charge transfer but also other processes can be rate determining steps, which have to be taken into consideration in case studies or planning.

5. The electrolysis

One of the technical realizations of charge transfer processes is the electrolysis [1, 6–8, 13]. Impressed current cathodic protection is also a technology based on electrolysis. We have also an electrolysis if we study a single electrode, because an auxiliary electrode is needed (in the field of pure sciences, however, do not bother too much about auxiliary electrode).

5.1. Mechanism of electric conduction

In the course of electric current, in an electric circuit made of a first order (electronic) and a second order (ionic) conductor, on the interface of the conductors of two types, chemical processes (charge transfer chemical processes) come into being. Explanation of this phenomenon is: from the first order conductor electrons are not capable to move out into the electrolyte, to move through the electrolyte and step into the other first order conductor. Electric current can be established in this kind of electric circuit, if at both of electrodes (at anode the oxidation, at cathode the reduction) electrode reactions take place [6–8, 13].

5.2. The thermodynamic condition of electric current

To carry out an electrolysis, a suitable electric tension is required, because electrode processes cannot be come into being with any kind of a small voltage [6–8]. Condition of an electrolysis is:

$$I_{\mathrm{el}} = \frac{E_{\mathrm{el}} - E_{\mathrm{d}}}{R_{\mathrm{ohm}}} \tag{11}$$

where I_{el} is electric current, E_{el} is voltage of polarization, E_{d} is the smallest decomposition voltage of material in the electrolyte, and R_{ohm} is the ohmic resistance of the cell.

In the course of an electrolysis, energy is added to the system, and the change of enthalpy:

$$\Delta H = \Delta G + T\Delta S \quad \text{or} \quad \Delta H = zFE + T\Delta S \tag{12}$$

Therefore, there is also entropy change ($T\Delta S$) in the course of an electrolysis. According to equation (12), ΔG can be given to the system electrolyzed by electric polarization, but entropy, $T\Delta S$ in the form of heat, also.

5.3. Diffusion to the electrodes

During the electrolysis the second condition of the electric current is the proper diffusion rate of reacting species to the electrodes [1, 1–8, 13]. The rate determining step very often is the diffusion, and in this case diffusion current can be measured.

The driving force of the diffusion is concentration gradient ($\partial c/\partial x$). If it is constant in time, then Fick's first law can be applied:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -Dq\left(\frac{\partial c}{\partial x}\right)_t \tag{13}$$

If concentration gradient changes in time, then Fick's second law must be applied:

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t . \tag{14}$$

In equations 'm' is the material that diffuses through 'q' cross-section, D is the diffusion constant (cm^2/s), 'c' is the concentration of the diffusing molecules, 't' is time and 'x' is distance.

6. Metal corrosion and the catalysis

Reaction rate of vast majority of the chemical reactions can be changed by the presence of some sort of an ingredient material. This material is called catalyst. Although there is a few example for catalytic acceleration of anodic process of metal corrosion, nevertheless, it is the experience that rate of anodic processes is difficult to influence, but the two most important cathodic processes of metal corrosion, hydrogen deposition, equation (4) and O_2 reduction:

$$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O \tag{15}$$

are sensitive to catalytic effects. In reality, these equilibriums do not exist without some catalyst [15, 16]. If these processes are the rate determining steps of metal corrosion then the rate of corrosion depends mostly on the rate of these cathodic processes, on the other hand, rate of these processes is the function of catalytic effects.

According to Horiuti [17], in rate equations (7) and (10) the magnitude of exchange current density is characteristic of catalytic activity of the surface. Explanation of this idea is that magnitude of the exchange current density depends on the chemical activation energy of the surface reaction, because in hidden manner it is in the exchange current, and otherwise, the magnitude of chemical activation energy is a function of catalytic activity.

Phenomena of bimetallic and multimetallic corrosion can be interpreted most on the basis of catalytic effects, for instance dissolution or corrosion of Pt–Zn couple in acidic environment [2].

6.1. Catalysts of hydrogen deposition

According to the results of metal catalysis, the smaller the hydrogen overvoltage on a metal, it is the better catalyst for reaction (4) [15]. The smallest the hydrogen overvoltage on platinum metals, but, for instance, on iron is also not too big, for this reason iron can be used as a catalyst in ammonia synthesis. Hydrogen overvoltage is huge on zinc, lead, cadmium, mercury, etc. In the case of metal corrosion, catalyst of process (4) either the corroding metal itself, or some impurity (for instance Cu, Pt (from cars)).

6.2. Catalysts for oxygen activation

Activation of oxygen is the condition of metal corrosion in the atmosphere. Process (15) is very complex, and very often it takes place through formation of H_2O_2 [8, 16, 18]. It turned out that in the course of iron rusting the corrosion product named lepidocrocite (γ-FeOOH) is the catalyst of oxygen activation [18]. Several materials are capable to activate oxygen, or dioxygen (O_2). Iron chlorides [16] and porphyrins deserve special attention. Porphyrins can be found in waste waters and good oxygen activators [19, 20]. Because of road salting, iron chlorides, and their oxygen activating character play an important role in metal corrosion.

As it has been proved, explanation of the polarity reversal of the Fe/Zn bimetallic corroding system is the result of the good oxygen activating (catalytic) character of the Zn corrosion products [21].

7. Mechanism of corrosion reactions

In spite of many new results, published in the last decades [18, 21–26], in the field of study of the mechanism of metal corrosion, in corrosion protection hardly rely in decisions on the scientific results [1]. Application of scientific results in solution of technologic problems diffuses slowly in the practice.

In general, the scientific results are preceded by the practice. For instance, dissolution of platinum accelerated by adsorbed gold, and palladium by adsorbed copper (chloride) was understood long after its industrial application [26]. At the rusting of iron, catalyst of oxygen activation is the already mentioned Fe^{2+} containing lepidocrocite [18]. In the course of iron dissolution in acids, the rate determining step is reaction (4) [25]. Recognition of this reaction step is also connected with catalytic effects [25].

7.1. Basis of bimetallic and multimetallic corrosion

The bimetallic and multimetallic corrosion processes can be arranged in three groups: an interaction destructing the passivity, another (catalytic) inter-action results in accelerating of either anodic or cathodic corrosion processes [27].

Destruction of the protecting passive layer can be made by application of proper chemical conditions (for instance HCl for chromium, or basic solutions for aluminum). Acceleration of metal corrosion can also be achieved by adsorbed (UPD, underpotential deposition) metals. This phenomenon can be experienced with Hg/Al couple. Not only

mercury can perform this effect. There are other metals which can also activate aluminum [28].

Hardly a few example is known for the acceleration of anodic processes. Practically, only the surface catalysts for chloride formation are known [26]. Catalytic acceleration of cathodic corrosion processes, however, is of a common knowledge. The hydrogen deposition and oxygen reduction are well known multistep catalytic processes [15, 16], if the second metal catalyses these processes, then the metal accelerates the corrosion of the first metal.

8. Adsorption phenomena in metal corrosion

Metal corrosion is a surface phenomenon, therefore, processes of corrosion can be influenced by intervention into the adsorption phase. For this reason, knowledge of metal corrosion and protection sometimes is based on the study of adsorption phenomena [29].

Two very important processes, O_2 binding and H_2 deposition have already been mentioned. Adsorption of metals on foreign metal surfaces (underpotential deposition (UPD)) and inhibitor adsorption play also a very important role in the field of metal corrosion [30, 31].

Study of adsorption phenomena is carried out via adsorption isotherms [29–31]. The most frequently measured isotherm is the Langmuir isotherm which based on the supposition that adsorption sites are the same, heat of adsorption independent of the coverage ($\Theta = \Gamma/\Gamma_{max}$, where Γ is the quantity of adsorbed material), there is no interaction between molecules of adsorbed material:

$$Bc = \frac{\Theta}{1-\Theta}. \tag{16}$$

In the case of Frumkin isotherm it is taken into consideration that adsorbed species can attract and repulse each other:

$$Bc = \frac{\Theta}{1-\Theta}\exp(-2a\Theta) \tag{17}$$

In the case of Temkin isotherm it is taken into consideration that adsorption sites are not the same, and by the increase of coverage, heat of adsorption is decreased:

$$Bc = \frac{\exp(a(\Theta)-1}{1-\exp[-a(1-\Theta)]}, \tag{18}$$

where B is the equilibrium constant of adsorption ($B = \exp(-\Delta G/RT)$), 'c' is the concentration of adsorbing material in the fluid phase, Θ is the coverage of adsorbed material, and 'a' the constant of interaction. Sometimes BET (Brunauer, Emmett, Teller) isotherms are also measured.

8.1. Adsorption of metals on foreign metal surfaces

In the course of development of surface chemistry it has been recognized that metals (Me) can adsorb on the surface of foreign metals (S), because the Me–Me bond is weaker than the Me–S bond (the phenomenon is called underpotential deposition (UPD)). Because of Me–S interaction, adsorbed metals oxidize at a more positive potential then their bulk form [30]. The difference is the so called underpotential shift (ΔU) caused by adsorption:

$$\Delta U = E_{\text{ads}} - E_{\text{N}} \text{ and } \Delta U > 0, \tag{19}$$

where

$$E_{\text{ads}} = E^0_{\text{ads}} + \frac{RT}{\gamma F} \ln \frac{a_{\text{Me}^{z+}}}{a_{\text{Me}_{\text{ads}}}}, \tag{20}$$

where E_{ads} is the adsorbed metal equilibrium potential, E^0_{ads} the standard potential of the adsorbed metal, γ is the electrosorption valency, $a_{\text{Me}^{z+}}$ is the activity of adsorbing ion in the electrolyte, and $a_{\text{Me,ads}}$ is the activity of the adsorbed metal in the adsorption phase. E_{N} is the electrode potential which can be calculated by the Nernst equation (3) (it is the so called Nernst potential).

Because of the UPD phenomena, the metals are apt to collect adsorbed foreign metal atoms on their surface, which results in change of their corrosion character. A well known technology mistake is the wire brushing with copper containing brush, which results in (adsorbed) copper contamination on the surface of a piece of work, for this reason, it is even more apt to corrosion.

Here must be drawn the attention to the bond between two dissimilar metals (for instance brazing and soldering, electroplated coatings, hot dip galvanizing, *etc*.), which starts with metal adsorption, and after this can take place interdiffusion, or alloy formation. There is no good adhesion without adsorption.

Adsorption of inhibitors is the condition of their corrosion protecting effect. Without adsorption there is no corrosion protecting effect of an inhibitor. Very often passivity comes into being by formation of also an adsorbed oxide layer [27–32].

8.2. Adsorption of inhibitors

In spite of surface chemical changes caused by any inhibitor, here, first of all we draw the attention to the character of organic inhibitors. Inhibiting effect is connected with their adsorption. Adsorption very often results in decomposition of organic molecule, in reality, not the given molecule, but its products of decomposition are the inhibiting species [31, 32].

Synthesis of organic inhibitors is the task of organic chemistry, their study, however, based on surface chemical and physical methods coming from catalysis or electrocatalysis.

8.3. Coatings

In manufacturing of different coatings, adsorption processes play an important role, because adhesion is also a surface chemical process. For the sake of completeness, the different coating methods have to be mentioned. The oldest one is the painting, then electroplating, hot dip galvanizing, and today chemical vapor deposition (CVD) and finally the physical vapor deposition (CVD) have to be mentioned.

9. Biological knowledge

Considering that there are living creatures which biological processes are causing corrosion, therefore, a corrosion expert must have biological knowledge. Bacilli, fungi, algae may form colonies on metal surfaces and in consequence of their metabolism, which may result in corroding chemicals, serious corrosion damage can be experienced. Most known organisms are the sulphate-reducing bacilli, for instance, desulphovibrio, desulphotomaculum, desulphomonas. These micro-organisms can reduce SO_4^{2-} ions and the product is H_2S [1, 31]:

$$SO_4^{2-} + 10H^+ + 8e \rightarrow H_2S + 4H_2O \qquad (21)$$

therefore, they contaminate their environs with hydrogen sulphide. There is a bacterium which capable catalyze oxidation of NO_2^- to NO_3^-, and in this way it destroys nitrite inhibitor.

The microorganisms play a similar role like a catalyst, because of biological interactions, activation energy of reactions in favour is decreased, similarly to catalytic effects.

10. The alloys

Textbooks and monographs deal mostly with pure metals. In the industrial practice, however, pure metals are rarely used, mostly alloys can be found. Corrosion behavior of alloys considerably differs from pure metals, therefore, a corrosion expert has to deal much with alloys [1–3, 6–8, 27].

In general, thermodynamic character of components of alloys differs also considerably. The less noble component can be leached, leaving behind the skeleton, or broken fragments of the noble component. Decomposition starts at a critical potential, therefore, potential of decomposition of an alloy is of basic questions. There is no decomposition at a relatively high electrode potential. The alloy components dissolve simultaneously. For instance, HNO_3 + H_2SO_4 mixture for brass washing or HNO_3 + HF mixture for stainless steel do not separate the components of the alloys.

The most common alloy decompositions are graphitization of cast iron, leaching of zinc from the brass, chromium from stainless steel, decomposition of alloys of aluminum, e.g., decomposition of aircraft aluminum, preparation of Raney catalysts.

11. Measurement knowledge

In study and practice of metal corrosion, the most frequently performed measurement is the measurement of electrode potential. These measurements can be separated into two groups. Measurement of equilibrium potential, and measurements of electrode potential in the course of a charge transfer reaction. The first measurement results in a thermodynamic, the other one is a reaction kinetic quantity, and in the course of electrode potential measurement during reaction very often a Luggin capillary is used.

A great many measurement and polarization technics have been developed and here the most frequently used will be mentioned [33].

11.1. Measurement of electrode potential

In the course of electrode potential, especially equilibrium potential measurements must be acted very carefully. It must be taken into consideration that the measurement takes place under atmospheric or deoxygenated circum-stances. It also must be taken into account that whether the measured metal forms an equilibrium system with the electrolyte, mostly water solutions? For instance, iron does not form equilibrium system with water solutions, because $E^0_{Fe^{2+}/Fe}$ = – 0.44 V, therefore, in the course of evaluation of results the interfering processes, the reduction of oxygen and the slow decomposition of water must be taken into account. Another very important point of view is that electrodes of second kind must not contaminate the electrolyte of the studied system.

Internal resistance of the voltmeter used for electrode potential measurements must be very high.

11.2. Measurement of electric current

It is the simplest task, and there is no difference between the amp-meters used in electric systems and in the field of metal corrosion.

11.3. The systems of polarization

In the field of electrochemistry several techniques of polarization have been developed. They are used in study and practice of metal corrosion [33]. Among them, there are two very important methods: the galvanostatic (constant current (I = constant)), and the potentiostatic (constant electrode potential (E = constant)) polarization. A special case of potentiostatic polarization is the potential sweep method, the cyclic voltammetry (dE/dt = constant). In this case the electrode potential is governed by a programmer.

12. Corrosion effects of electric energy systems

The electric energy system and electric traction may have a profound effect on appearance and proceeding of metal corrosion. The influence can be experienced both in direct and alternating current systems. It is well known the strong influence of stray currents and high voltage long-distance transmission lines on the processes of metal corrosion. Stray current

is mostly the result of electric railways, the electric traction. The corrosion by alternating current, however, is the harmful effect of high voltage transmission lines.

Summary

Metal corrosion is a charge-transfer chemical process. Its research and the metal corrosion protection require manifold knowledge in the field of thermodynamics, reaction kinetics and catalysis, transport and surface phenomena and adsorption. Knowledge of dealloying processes and biocorrosion is also very important in this field. It is to be taken into account that for both the study of metal corrosion and the corrosion protection require reliable measurements and data. Finally, the corrosion effects of electric railways and energy systems on metals must also be taken into consideration.

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