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Metals and Corrosion

Morten Stendahl Jellesen

2.1 Introduction

Corrosion is a natural phenomenon for metals. In accordance with the laws of thermodynamics, metals after production and shaping return to their lower energy state: metal ore. Corrosion is the electrochemical dissolution of metals during which metals are released together with electrons (the oxidation process). At the same time, electrons are consumed (the reduction process). In total, the corrosion process is an irreversible reaction. Equation 2.1 shows the anodic reaction, i.e., metal oxidation, and Equation 2.2 the cathodic (reduction) reaction if the process takes place in an acidic environment (involving a reduction of H+). Equation 2.3 shows the reduction processes taking place if the corrosion process happens at neutral or alkaline electrolyte systems (involving a reduction of O_2, i.e., oxygen from the atmosphere or dissolved in the aqueous electrolyte).

$$M \rightarrow M^{n+} + n\,e^{-} \tag{2.1}$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \tag{2.2}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{2.3}$$

The anodic and cathodic reactions take place on the same metal surface, meaning that if the cathodic reaction is reduced, then also the anodic reaction is reduced in order to satisfy the conditions of having a zero net current. This means that corrosion can be limited by not only protecting the metal from anodic dissolution but also by reducing the reduction reaction (e.g., by limiting the amount of oxygen).

In a system with a metal and an electrolyte, several corrosion reactions can take place, with metal oxidation into metal ions (Equation 2.1) representing just one of them. This oxidation reaction leads to the formation of free ions that can diffuse into surrounding solution or become involved in the formation of metal oxides, metal chlorides, organometallic compounds, or other chemical species. In practice release of metals rarely happens as active dissolution resulting in free metal ions but as a more complex process involving passivation of the metal with metal release because of passive dissolution and transpassive dissolution or due to local corrosion phenomena happening on the metal surface. A general schematic of reactions taking place at a passive metal surface is given in Fig. 2.1.

For many metals and alloys, their stability is due to the formation of a thin oxide layer (the passive layer). Examples are aluminum (Al), titanium (Ti), and stainless steel (chromium (Cr)). The passive layer is spontaneously formed with

M.S. Jellesen
Department of Mechanical Engineering,
Technical University of Denmark, Produktionstorvet,
Building 425, Room 028, 2800 Lyngby, Denmark
e-mail: msj@mek.dtu.dk

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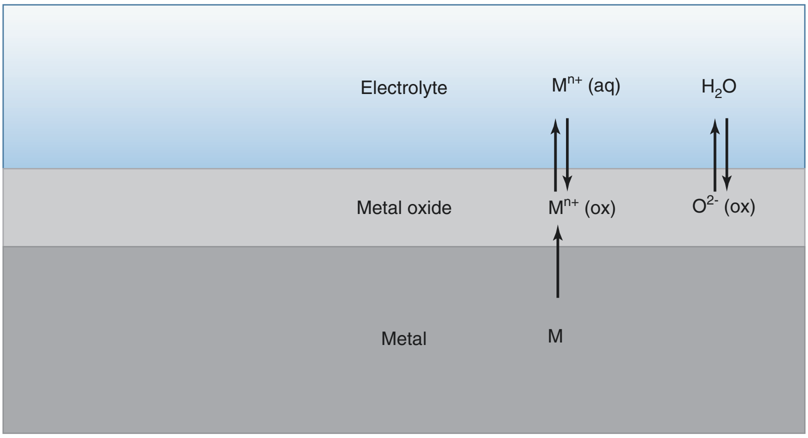

Fig. 2.1 Schematic of electrochemical reactions of a passive metal. Metal cations are generated in the interface of metal and oxide, and the ions migrate through the passive film and across the passive film/electrolyte interface. Anions of O^{2-} migrate from the electrolyte interface toward the metal. The overall result is the generation of a passive film on the metal surface

surrounding oxygen and protects against the environment. The protective properties of the passive film are due to the passive film acting as both an electronic barrier for electrons and also a physical barrier for cation and ion transport to the metal surface in the electrolyte. Known passivating metal alloys are stainless steel (chromium oxide), titanium, and aluminum alloys.

The degree of protection is determined by the rate of ion transfer through the film, as well as the stability of the protective film against dissolution. Chemical composition, structure, thickness, homogeneity, and the presence of defects are important parameters determining the level of protection that a passive film provides against metal dissolution. As for all corroding systems, the chemical composition of the electrolyte (especially pH and chloride content), the redox condition, exposure time, and temperature are also important parameters affecting the level of corrosion.

In some cases, transpassive dissolution can happen. This is when the protecting passive film is oxidized further into higher oxidation levels. Examples are biomaterials exposed to highly oxidizing media such as hypochlorite or hydrogen peroxide, in which the risk of forming Cr^{6+} in the transpassive region has attracted attention due to the high toxicity and carcinogenicity of Cr^{6+} [1].

Metals that do not form passive films are in their active or immune state. If electrochemical conditions are such that a metal is in its active state, this means that the metal forms a charge transfer reaction at the metal electrolyte with the result that the metal ions are released into the solution as ions (Equation 2.1). If the solubility of the metal ions in solution close to the surface is exceeded, a precipitation of corrosion products will occur on the metal surface.

Many corrosion attacks seen on passive materials are due to only localized corrosion attacks, where the remaining surface has an intact passive layer. The mechanism for localized corrosion is self-propagating, since a local site for anodic dissolution can alter the local electrolyte environment, and at the same time, there is a large area of the metal surface available for the corresponding cathodic reduction reactions. Pitting and crevice corrosion of stainless steel are well-known examples of local corrosion being accelerated at low pH in environments with a high amount of chlorides (Fig. 2.2).

2.2 Thermodynamic Considerations

The thermodynamic calculations for the stability of passive films on various metals can be illustrated in Pourbaix diagrams, known as potential-pH diagrams [2]. The schematic Pourbaix diagram given in Fig. 2.3 shows the regions of active dissolution, passivation, and immunity.

Fig. 2.2 The pictures to the *left* show crevice corrosion under a gasket in a stainless steel heat exchanger, and to the *right*, a stainless steel railing for a staircase leading into a swimming pool. In both cases, corrosion is initiated due to high chloride content and stagnant conditions in the crevice formed when assembling against polymer gaskets

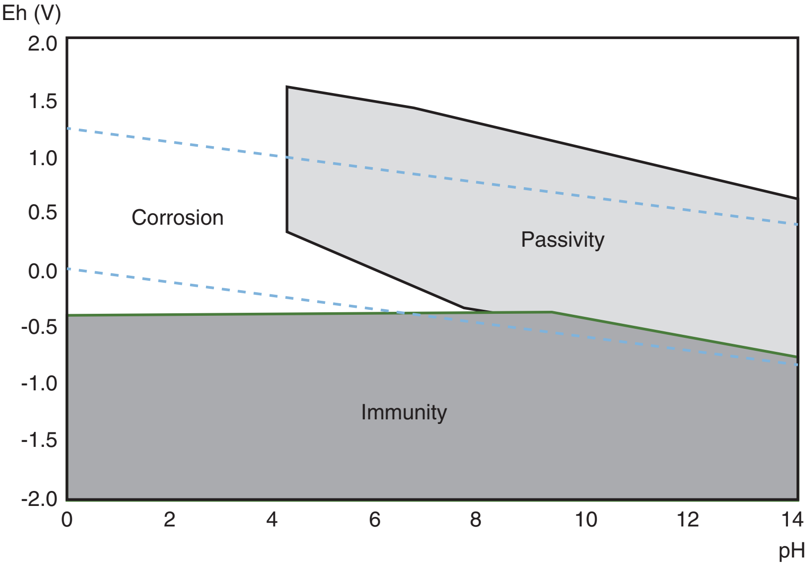

Fig. 2.3 Schematic Pourbaix diagram for stainless steel showing the regions of immunity, corrosion (active and transpassive dissolution), and passivation at varied pH and electrochemical potential regions. The *dotted blue lines* show the stability region of water

The tendency for individual metals to accept or donate electrons is given in the electrochemical series (Fig. 2.4). The higher E^0, the more noble the metal. Among the best known noble metals are gold (Au), silver (Ag), or platinum (Pt). The electrochemical series is given as calculated standard potentials at standard state conditions, meaning a concentration of 1 M at 25 °C. A change in electrolyte or temperature will change the potential values, e.g., gold is soluble in aqua regia (a mixture of nitric acid and hydrochloric acid), due to nitric acid being an oxidizer and chloride ions forming soluble complexing ions with gold.

Nickel and iron are examples of metals being less noble, with the least noble metals being zinc and magnesium. Due to the negative electrochemical potential of these metals, they can protect the less active metal to which they are coupled. This property is utilized when zinc and magnesium metals are used as sacrificial anodes for the protection of constructions or ships.

2.3 Electrochemical Studies of Corrosion Kinetics

In order to get a deeper understanding of a specific metal's corrosion properties, laboratory studies are commonly carried out. Electrochemical techniques, such as open circuit potential monitoring, potentiodynamic curves, and potentiostatic tests, can be carried out with a potentiostat as hardware and a three-electrode system. The three-electrode system consists of the metal as a working electrode, a reference electrode, and a

Electrode	E°/V
$Li^+ + e = Li$	– 3.045
$Ca^{2+} + 2e = Ca$	– 2.84
$Na^+ + e = Na$	– 2.714
$Mg^{2+} + 2e = Mg$	– 2.356
$Al^{3+} + 3e = Al$	– 1.67
$Ti^{2+} + 2e = Ti$	– 1.63
$Mn^{2+} + 2e = Mn$	– 1.18
$Cr^{2+} + 2e = Cr$	– 0.90
$Cr^{3+} + 3e = Cr$	– 0.74
$Zn^{2+} + 2e = Zn$	– 0.76
$Fe^{2+} + 2e = Fe$	– 0.44
$Cd^{2+} + 2e = Cd$	– 0.403
$Ni^{2+} + 2e = Ni$	– 0.257
$Mo^{3+} + 3e = Mo$	– 0.20
$Sn^{2+} + 2e = Sn$	– 0.136
$Pb^{2+} + 2e = Pb$	– 0.125
$Cu^+ + e = Cu$	0.520
$Hg_2^{2+} + 2e = 2Hg$	0.796
$Ag^+ + e = Ag$	0.799
$Pd^{2+} + 2e = Pd$	0.915
$Pt^{2+} + 2e = Pt$	1.188
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$Au^{3+} + 3e = Au$	1.52
$Au^+ + e = Au$	1.83

Fig. 2.4 Standard potentials of electrode reactions

counter electrode (Fig. 2.5). The purpose of the reference electrode is to measure the potential. The counter electrode is typically made of corrosion-resistant materials such as platinum or graphite, and its function is to act as the counterpart in the electrical circuit with the working electrode. With this configuration the potential of the working electrode can be measured against a reference electrode, and the potentiostat can monitor the current in the circuit while regulating the potential between the working and the reference electrode.

With a reference electrode and the metal of interest immersed in the same electrolyte, the open circuit potential can be monitored. The open circuit potential is the potential of a metal in a given electrolyte and in the absence of any applied external current, e.g., by a potentiostat. At the open circuit potential, the anodic and cathodic reactions occur simultaneously and at the same rate. Typically the open circuit potential is measured prior to further electrochemical studies in order to give the metal time to stabilize in the electrolyte. The open circuit potential measurement is useful since it provides information on the surface conditions of the metal in contact with the electrolyte, similar to the standard potential values given in Fig. 2.4, although in this case the potential value represents the actual metal (alloy) and a given electrolyte at a given temperature. The open circuit potential value as such represents the possible chemical reactions taking place at the surface, e.g., passivation reactions as sketched in Fig. 2.1, and the formation rate of a passive film can be monitored. The open circuit potential value increases until a steady-state value is reached as the metal is fully passivated.

A potentiodynamic measurement using all three electrodes gives the option of measuring the current density as a function of the applied potential, as the potential (viz., the reference electrode) is changing at a constant rate by the potentiostat. The result is a collection of both current density and potential data as shown in Fig. 2.6. Performing an open circuit potential measurement and creating a potentiodynamic curve are typically the first approach when studying a metal alloy in a given electrolyte. ASTM G5-94 [3] establishes a standard for measuring potentiodynamic curves where experimental conditions such as scan rate are suggested. It is important that the scan rate is sufficiently slow in order to permit steady-state mass transport conditions at the electrode surface.

As the anodic polarization scan starts, an increase of current density is seen. This part of the potential scan is where the metal is in its active state and is characterized by dissolution of the metal and formation of soluble ions that dissolve into the solution. The current density values monitored in this part of the potential scan can be

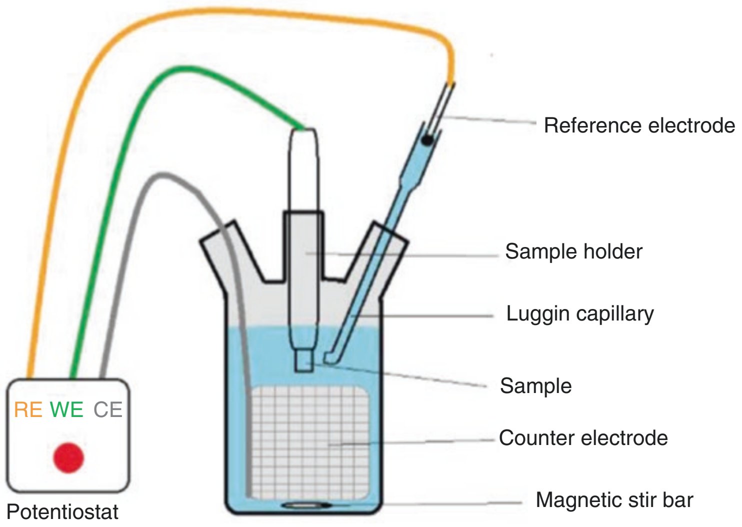

Fig. 2.5 Electrochemical measurement setup including potentiostat with connection to reference, working, and counter electrode. The setup allows for corrosion monitoring at various electrochemical potentials for different metal alloys, electrolytes, and temperatures

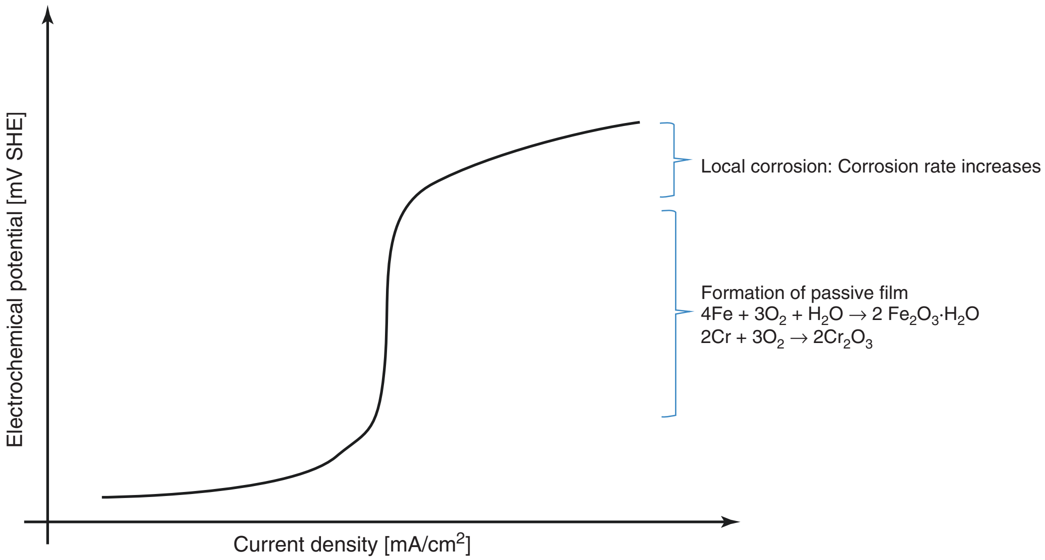

Fig. 2.6 Schematic representation of the anodic part of a polarization curve made on stainless steel in a nonaggressive electrolyte solution by the use of potentiodynamic measurement via a potentiostat and three-electrode setup. As the electrochemical potential is increased, the current density is monitored and represents passive layer formation (chromium and iron oxide for stainless steel) and shows the electrochemical potential where local corrosion is initiated

directly related to the corrosion rate of the metal in the electrolyte system via Faraday's law.

$$m = \frac{I \cdot M \cdot t}{n \cdot F} \tag{2.4}$$

In Faraday's law (Equation 2.4), m is the mass of metal dissolution over time, t and I are the anodic current, n the number of electrons, and F Faraday's constant (96,485 (C/mol).

As the potential is increased, the surface of the metal is covered by a passive film that decreases metal dissolution and thus current density. The passivation region is typically characterized by its passivation potential value (the initiation of passivation) and the current density value of the passive region, representing the current density that runs through the metal and oxide as sketched in Fig. 2.1. The passivation current density thus represents the protective properties of the film: the lower the current density, the more protective the film is against dissolution.

At high electrochemical potentials, there can be local breakdown of the passive film (e.g., pitting corrosion of stainless steel in a chloride-containing electrolyte). This transpassive region of the polarization curve is characterized by increased current density; however, the total current can no longer be ascribed to metal dissolution or oxidation of the metal. If the electrochemical potential in the transpassive region is higher than the potential for water, some of the current running in the three-electrode setup will be a result of oxygen evolution due to water oxidation.

The placement of a given metal in the electrochemical series or the thermodynamic state illustrated in the Pourbaix diagram, together with experimental analysis using potentiostatic measurements, is the basis for describing a metal's interaction with any given electrolyte system. Whereas Pourbaix diagrams will supply thermodynamic information on the metal electrolyte interface, potentiostatic testing provides information on the kinetics of metal dissolution. More detailed studies can be performed with potentiostatic tests in order to evaluate the specific effects of factors such as temperature, chloride content or electrochemical potential on the structure, composition and thickness of formed passive layers, or active dissolution of metal.

2.4 Summary

Corrosion is the electrochemical dissolution and release of metals that occurs when a redox reaction takes place. Metal release can be directly related to the oxidation of a metal; however, many metals and alloys form a thin oxide layer that passivates the surface and decreases metal release. The degree of protection is determined by the rate of ion transfer through the passive film, as well as the stability of the protective film against dissolution. This lack of protection at high chloride containing environments explains the well-known examples of crevice or pitting corrosion seen for stainless steel in, e.g., a swimming pool environment. The state of a metal, whether it is in its active dissolution, passive, or immune state, can be thermodynamically illustrated by Pourbaix diagrams, showing the effects of electrochemical potential and pH. Corrosion kinetics and resulting metal release can be determined by electrochemical laboratory measurements.

References

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3. ASTM G5 – 94. Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements. West Conshohocken, PA: ASTM International; 2011.