

FUNDAMENTAL ASPECTS OF CORROSION OF METALLIC MATERIALS

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Keywords: Metals, Alloys, Surface, Corrosion, Anodic dissolution, Passivation, Pitting, Thin Oxide Films, Electronic properties, Structure, Segregation, Aging, Chloride, Sulfur

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Summary

The understanding of the fundamental mechanisms of corrosion of metallic materials in

aqueous solutions requires the investigation, at the molecular or atomic level, of the surface reactions leading to corrosion or protection against corrosion of metals and alloys. These surface reactions are: (a) the anodic dissolution which is the fundamental reaction of corrosion, (b) the adsorption of various species found in the environment which are susceptible to modify the reactivity of the metallic surface, (c) the growth of hydroxylated oxide films that protect the underlying substrates against corrosion (passive films), and (d) the local breakdown of passive films which can lead to localized corrosion. On passivable metals and alloys such as stainless steels, passivation results from the growth on the surface of nm-thick layers of oxides or oxihydroxides. The knowledge of the growth mechanisms, the structure and chemical composition of these ultra-thin layers is necessary to control their long-term resistance in chemically aggressive media.

This article focuses on experimental data obtained by modern surface science techniques and emphasizes the competition at the atomic level between the reactions of anodic dissolution and passivation at metallic surfaces, the role of the surface structure and adsorbed species in these reactions, the chemical composition, crystallinity and defects of passive films, their electronic properties, the mechanisms leading to passivity breakdown and localized corrosion (pitting), the role of aging under polarization on the composition and crystallization of passive films, the mechanisms by which alloying elements are beneficial and some environmental elements that can be detrimental to the corrosion resistance.

1. Introduction

Corrosion is the degradation of metallic materials under the effect of the environment. This is a surface reaction that propagates progressively affecting the integrity of the material. In liquid water, or in the presence of a condensed water layer on the surface, corrosion leads to the formation of corrosion products, and to a progressive generalized or localized loss of matter. The surface reaction is of an electrochemical nature, involving exchanges of charge and matter at the solid (metal)/liquid (water) interface. Two types of electrochemical reactions take place simultaneously: an anodic reaction, in which the metal is ionized and the cation thus formed goes into solution where it is hydrolyzed; and a cathodic reaction in which the electrons produced in the anodic reaction are consumed in the reduction of protons in hydrogen or in the reduction of the oxygen dissolved in water, among other possibilities.

Corrosion science, whose aim is to understand corrosion phenomena, is strongly interdisciplinary. It involves materials science, metallurgy, surface science, electrochemistry and mechanics.

From an historical point of view, corrosion has been and is observed in all civilizations in which technology has been and is widely dependent on the use of metals and alloys. Indeed, all metals, except for some noble metals such as gold, are subject to corrosion. Thus, the surface of bronze is progressively covered by patina, the surface of iron rusts, and even if modern alloys such as stainless steels, nickel-based stainless alloys, or aluminum alloys, have a better resistance to corrosion, they are still affected by corrosion.

Nowadays, corrosion of metallic materials remains a technological and major economical challenge. The lifetime of products containing metallic components is often limited by the corrosion of their metallic parts. The cost of corrosion of metals and alloys is generally estimated to about 4% of the gross domestic product and one estimates that 25% of this cost could be saved with a better understanding and control of corrosion phenomena.

This justifies the intense R&D activity all around the world in public research laboratories (universities, national research centers) and in private research laboratories belonging to a wide field of industrial sectors: metallurgical industries, automotive industries, aeronautics, chemical industries, energy production, microelectronics, just to give a few examples. The results of these research investigations are published in international scientific journals and are the subject of many symposiums. National and international scientific societies promote the field.

Strategies of corrosion prevention have to take into account the material-environment couple (environment being defined by service conditions in the broad sense of the term, including storage conditions for example) and also the economical aspects of production cost, maintenance and lifetime. Furthermore ecological aspects are becoming more and more important, e.g., new standards limiting the use of certain metals because of production processes or particular applications, growing importance of industrial waste control and recycling.

The technological choice of the material can be made according to different criteria:

- Material having a sufficiently low corrosion rate: for example, in the case of steel structures, the lifetime of which will be long enough according to their corrosion rate.
- Use of passivable metals and alloys: these more sophisticated materials are covered by an ultra thin layer at the surface which protect them against corrosion; thus such materials are auto-protected against corrosion. Their cost is of course higher and their use restricted to products with higher added value than steel structures.
- Implementation of additional means of corrosion protection on materials which would otherwise poorly resist corrosion in service conditions: organic or inorganic corrosion inhibitors, chemical conversion treatment, coatings, cathodic protection.

The objective of this article is to give the readers the basis that will enable them to understand the reactions of electrochemical corrosion, including the fundamental reactions of corrosion, their kinetic and thermodynamic aspects. Metals and alloys passivation is presented in a detailed way: chemical composition, atomic structure, electronic properties and growth mode of passive layers. It is actually a field where recent research has enabled the elucidation of the mechanisms at a microscopic scale, a scale at which interactions between atoms and molecules take place. Localized corrosion of passivable metals and alloys is then discussed. Finally, the role of alloying elements is explained, particularly in the case of stainless steels. As a general rule, this article aims to show the relations that exist between microscopic forces and macroscopic effects of corrosion.

2. Electrochemical Characteristics of the Corrosion of Metallic Materials

2.1. Anodic Polarization Curves

The electrochemical corrosion of metals and alloys can be conveniently described by the schematic current-potential curve shown in Figure 1. Such a curve is also referred to as a potentiokinetic or anodic polarization curve.

Three regions can be distinguished in this curve. The first region corresponds to the active state of the metal, where anodic dissolution takes place, according to the following global reaction



where M denotes the metal atoms on the surface that pass into the aqueous solution in the form of cations (which are then hydrolyzed). A number, n , of electrons are exchanged in this electrochemical reaction. In this region (the ascending part of the peak), the current density is an exponential function of the potential according to classical electrochemical kinetics. Atomistic aspects of the mechanisms of anodic dissolution are presented in Section 3.

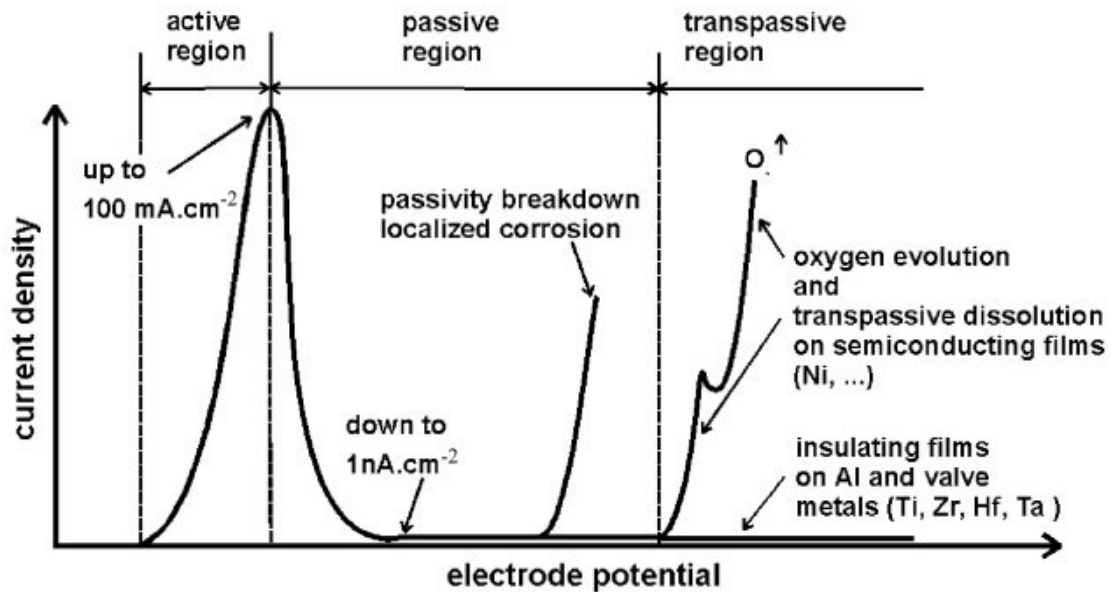
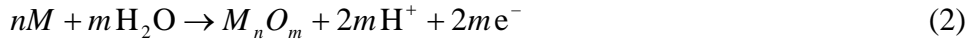


Figure 1. Anodic Polarization Curve (Current Density vs. Potential) of a Metallic Material Showing the Regions of Active Anodic Dissolution, Passivity and Transpassivity. For semiconducting passive films, the passive region extends over one Volt or less. For the insulating films formed on valve metals, the passive region extends over a few Volts before dielectric breakdown. Passivity breakdown and localized corrosion usually occur in the presence of aggressive ions (e.g., Cl^-)

The second region, which is observed in Figure 1 for metals that can be passivated, corresponds to the passive state of the metal. It starts with a transition from the active to the passive state, which is responsible for the peak appearing in the current-potential

curve. Above the critical passivation potential corresponding to the maximum in the active peak, an oxide (or oxyhydroxide) film grows on the surface and the dissolution current drops to a value which is typically several orders of magnitude lower than the anodic dissolution current at the maximum of the active peak. It is said that the metal surface is passivated, or that the material is in the passive state. The anodic reaction of oxidation is:



The passive region usually extends over a significant range of potentials (a few hundreds of mV). Atomistic aspects of the mechanisms of passivity are presented in Section 4.

The third region in the polarization curve is the transpassive region in which, when the potential is further increased, the current density begins to rise. In this region, increased dissolution of the material (under conditions where electrochemical polishing can be performed) takes place. On passive films with appropriate semiconducting properties, oxygen evolution can occur:



In the case of Al and other metals such as Ta, Zr, Nb, Ti... (usually denoted valve metals), the surface oxide films are insulating and they become thicker with increasing potential. In this case, oxygen evolution does not take place and the passive region extends over a few Volts before dielectric breakdown of the oxide film occurs.

When impurities or aggressive anions (e.g., Cl^-) are present in the aqueous solution, an increase in the current density can be observed at a potential located in the passive region (i.e., below the transpassive potential). This effect is caused by local breakdown of the passive film and localized dissolution. The initial stages of this important phenomenon, usually called pitting corrosion, will be discussed in Section 5.

The effects of alloying elements on anodic dissolution, passivation and pitting corrosion are discussed in Section 6.

2.2. Cathodic Reaction

It is important to note that the anodic (oxidative) reactions described above are half reactions, which means that a cathodic (reductive) reaction must take place simultaneously on the surface to satisfy the conditions of zero net current. The cathodic reaction may be the reduction of protons from the solution



or the reduction of oxygen dissolved in the aqueous solution



Electrochemical instruments (potentiostat) allow us to investigate separately the anodic and the cathodic reactions, the anodic reaction occurring on the studied metal surface and the cathodic reaction on a counter electrode, the potential being set with a third electrode (the reference electrode). In practical situations, both the anodic and the cathodic reactions take place on the material surface. This is an important point because it can be immediately understood that although the fundamental reaction of corrosion is the anodic dissolution, it involves necessarily a cathodic reaction (which can thus be used in some cases as a mean of controlling the corrosion rate).

2.3. Thermodynamic Aspects of Corrosion and Passivity

The above considerations were based on the polarization curve, which is a kinetic approach to anodic dissolution (or corrosion), passivation and transpassivity. Obviously, the associated chemical reactions take place only if they are permitted by thermodynamics. As regards to passive films, two cases can be distinguished, depending on whether the oxide film on the surface is, or is not, in equilibrium with the aqueous solution at a given potential and pH.

In some cases, e.g., Cu, the existence of the passive film in equilibrium with the aqueous solution is predicted by thermodynamics, and this can be easily visualized in diagrams showing the domains of stability of different species as a function of potential and pH. These diagrams, known as potential-pH (E-pH) diagrams, or Pourbaix diagrams, have been calculated for several metals. Figure 2a shows the potential-pH diagram for copper in water at 25 °C. The formation of a passive film of cuprous and cupric oxides is predicted.

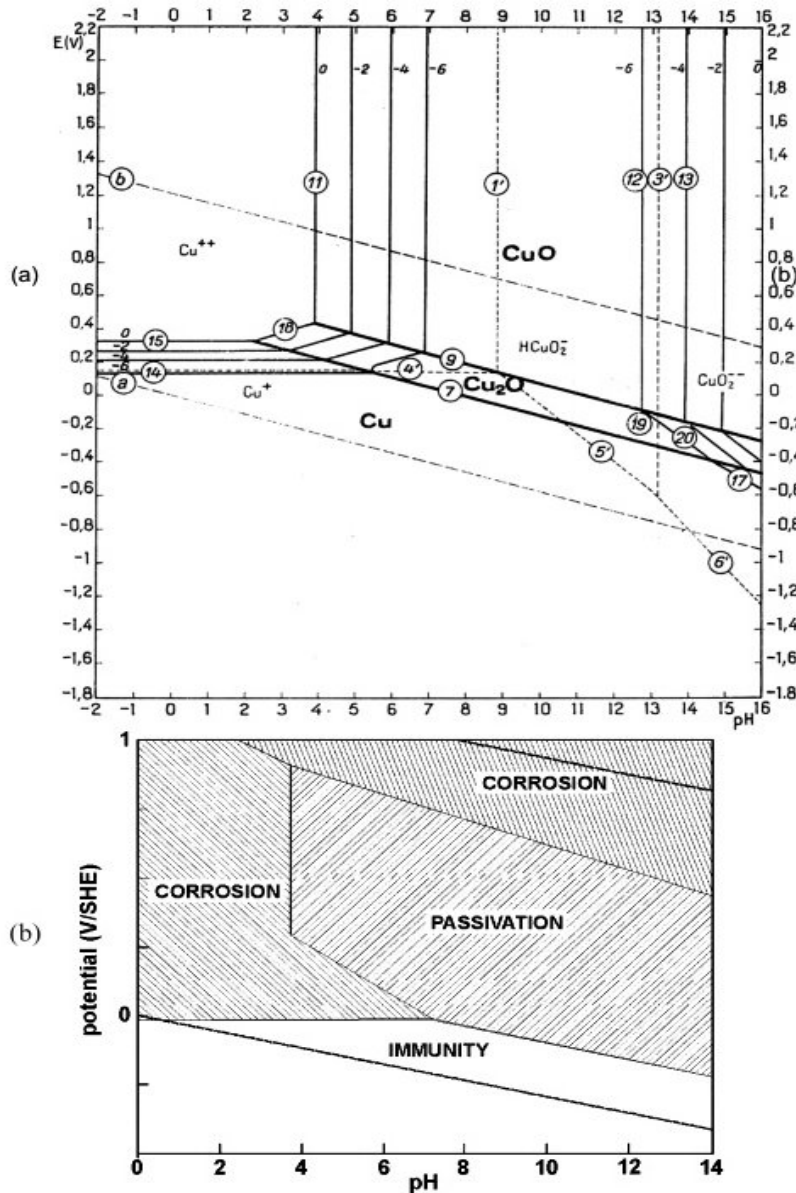


Figure 2. (a) Potential-pH Diagram of Cu in Aqueous Solution at 25 °C

The lines a and b indicate the domain of thermodynamic stability of water. The formation of Cu₂O and CuO is predicted in the marked regions. (Source: Pourbaix M. (1963). *Atlas d'Equilibres Electrochimiques*, (ed. Cebelcor) Paris: Gauthier-Villars). (b) Schematic potential-pH diagram showing the regions of immunity, corrosion (active and transpassive dissolution) and passivation

In the case of many metals which can be passivated, e.g. Fe, Ni and Cr, passivation in acidic solution does not result from a thermodynamic equilibrium, but from the fact that the dissolution rate of the oxide in the acidic solution is very slow. Figure 2b shows a schematic potential-pH diagram for metal-water systems. A passive film, not in equilibrium, but dissolving slowly, may exist in the region of the E-pH diagram denoted by corrosion. The region denoted by immunity corresponds to conditions in which the metal is stable (no dissolution takes place). The more or less protective character of the

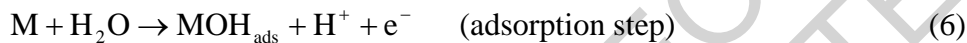
passive film cannot be derived directly from such diagrams.

3. Anodic Dissolution in the Active State

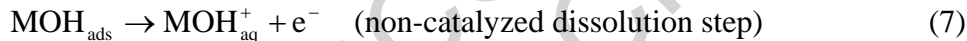
3.1. Mechanisms of Anodic Dissolution

Anodic dissolution proceeds via the formation of chemical bonds between surface atoms and solution species (solvent molecules and ions). The elucidation of the mechanisms of anodic dissolution consists in identifying the intermediates species formed on the metal surface and their kinetic role in the irreversible reaction leading to stable cationic species dissolved in the solution. The complex pH, anion and potential dependence of the dissolution rate observed experimentally is assumed to reveal the competitive role of the different mechanisms involving the metallic elements in various oxidation states and anion and solvent species of the solution.

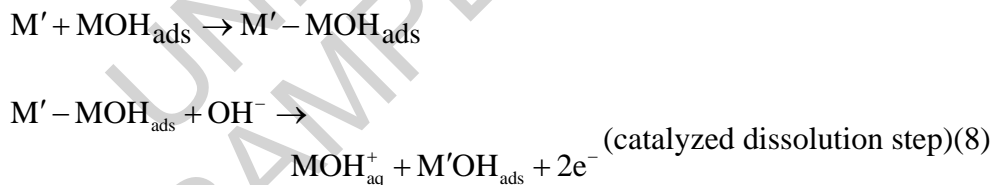
Several mechanisms operating competitively are generally considered. They take place after a common adsorption-hydrolysis step leading to MOH_{ads} intermediate species:



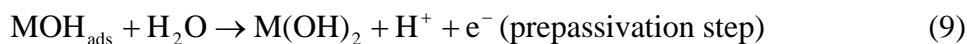
The metal atoms bonded to hydroxyl ligands can then dissolve according to the hydroxo-ligand mechanism. In the dissolution step, the dissolving atom can maintain its bond with the solution species, this is the so-called non-catalyzed or consecutive mechanism:



The dissolving atom can also translate its ligand to a first nearest neighbor (M'), this is the so-called catalyzed or catalytic mechanism:



There is also a competitive branching to prepassive and passive states:



These mechanisms have been studied in detail for iron. The reaction paths found in acidic media are illustrated in Figure 3. The $\text{K}_1\text{-K}_2$ path is the non-catalytic mechanism operating at low pH and low current density (i.e., low potential). The $\text{K}_1\text{-K}_3\text{-K}_4$ path is a catalytic route operating in the ascending part of the anodic peak at higher current density and at higher pH. The $\text{K}_1\text{-K}_5\text{-K}_6$ path is the main dissolution route (catalytic type) of Fe(II) species operating at still higher pH and higher current densities (i.e., higher potential). Fe(II) species are dissolved. The route leading to Fe(II) prepassivating

and Fe(III) passivating species branches from the Fe(II)_{ads} intermediate species. These different paths illustrate the dependence of the mechanisms of anodic dissolution on the pH and potential.

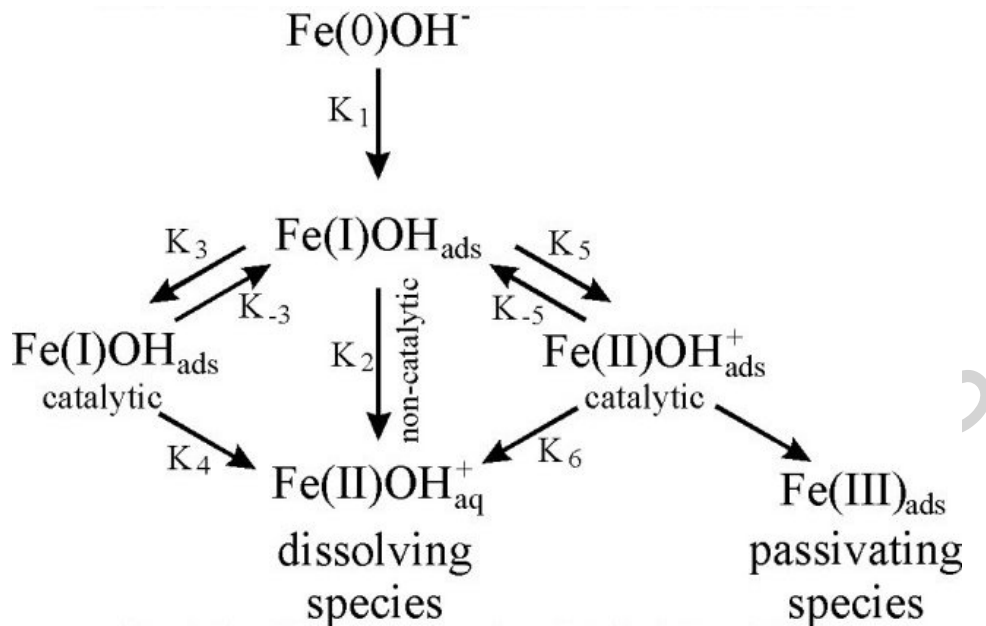
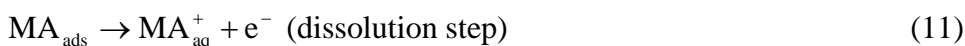


Figure 3. Non-catalytic and Catalytic Reaction Paths Leading to the Anodic Dissolution and Passivation of Iron in Aqueous Solutions

The mechanisms of anodic dissolution of other metals are not so well established. Cobalt seems to behave similarly to iron with formation of a Co(I)OH_{ads} catalytic surface species. In contrast the mechanism of anodic dissolution of nickel is quite controversial. As far as chromium is concerned, the non-dependence on pH of the active dissolution rate is indicative of less complex dissolution routes than for iron. The dissolution route is similar to the K₁-K₂ path in Figure 3 with Cr(I)OH and Cr(II)OH⁺ adsorbed intermediates leading to the dissolution of Cr(II) species and branching to Cr(II)_{ads} prepassive states that may also dissolve. H₂ evolution is thought to take place simultaneously.

The contribution of anions other than hydroxyls is commonly experienced through the dependence of the dissolution on the electrolyte composition at a given pH. The metal atoms can be dissolved bonded to anion ligands (A) according to the anion-ligand mechanism:



Dissolution in the active state can differ from the hydroxo-ligand mechanism in the presence of anions able to strongly bond to metal atoms. Mixed adsorbed intermediate species, (M(OH)₂)_{ads}, (M(OHA))_{ads} and (M(A)₂)_{ads}, have been proposed to play a role in the case of iron in acetate solutions. The competitive adsorption between halide ions

and hydroxyls largely dominates the active dissolution of iron and other metals in the presence of halide ions. For iron in HCl-NaCl media, a pattern similar to that in Figure 3 with consecutive and catalytic dissolution paths branching from $\text{Fe}(\text{I})\text{OH}_{\text{ads}}$ species but with a third path (non-catalytic type) involving $\text{Fe}(\text{I})\text{ClOH}^-$ intermediate species has been proposed. A gradual increase of the Cl^- content initially reduces the contribution of the K_1 - K_5 - K_6 catalytic path in favor of a catalytic step similar to K_1 - K_3 - K_4 , the intermediate species being $\text{Fe}(\text{I})\text{Cl}_{\text{ads}}$ instead of $\text{Fe}(\text{I})\text{OH}_{\text{ads}}$.

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Biographical Sketches

Philippe Marcus is Director of the Laboratoire de Physico-Chimie des Surfaces, Centre National de la Recherche Scientifique, Ecole Nationale Supérieure de Chimie de Paris, Université Pierre et Marie Curie (Paris VI), France. Dr. Marcus received his Ph.D. in Chemistry from the Université Pierre et Marie Curie in 1979. He has written over 200 scientific papers in the fields of Corrosion Science, Surface Chemistry, Surface Analysis and Materials Science. He is the co-author or co-editor of several books and book chapters, including *Corrosion Mechanisms in Theory and Practice*. Dr. Marcus is a member of the Editorial Board of *Corrosion Science* Journal and of *Materials and Corrosion*. He is chairman of the EFC (European Federation of Corrosion) Working Party on *Surface Science and Mechanisms of Corrosion and Protection*, co-chairman of Division 6 of ISE (International Society of Electrochemistry) on *Corrosion, Electrodeposition and Surface Treatment*, and chairman of the Science and Technology Committee of CEFRACOR (Centre Français de l'Anticorrosion).

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