Fundamentals of Electrochemical Corrosion

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Cover art represents autocatalytic processes occurring in a corrosion pit. The metal, M, is being pitted by an aerated NaCl solution. Rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. Source: U.R. Evans, Corrosion, Vol 7 (No. 238), 1951

Dedication

To my wife, Bernice; daughters, Ginny, Kate, and Barb; and son, Dave.

Gene Stansbury

To my wife, Billie; daughter, Karen; mother, Katherine; and in memory of my son, Mike.

Ray Buchanan

And to our graduate students who have extended our understanding of this fascinating field.

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Preface

The objective of this book is to provide a reasonably self-contained textbook covering the essential aspects of the corrosion behavior of metals in aqueous environments. It is designed to be used in courses for upper-level undergraduate and graduate students, for concentrated courses in industry, for individual study, and for reference. It has been our experience that both students and persons in industry come to a first course in corrosion with a wide diversity of backgrounds, both academically and in terms of experience in corrosion behavior. The usual pedagogical problem arises as to the minimum background for each participant allowing a useful understanding of the subject. This text has been designed to provide flexibility in meeting this need.

An introductory chapter, Chapter 1, provides an overview of aqueous corrosion. Emphasis is placed on the fact that corrosion is an interface phenomenon and, as such, is dependent on the variables defining the metal, the environment, and the physical aspects of the interface itself. Schematic electrochemical cell circuits are used to illustrate how these variables give rise to electrical potential differences across the interface and drive the corrosion process, resulting in current densities directly related to the corrosion rate. The fact that the current is also controlled by interface films allows emphasizing how passive-type alloys with their adherent oxide films have lower corrosion rates than the nonpassive alloys.

The essential electrochemical background is provided in Chapter 2 on electrode reactions and in Chapter 3 on electrode kinetics. These chapters contain the essential electrochemical concepts required for understanding the following chapters. Chapter 2 covers the principles governing the stability of metal/environment systems. Following an introduction to the classical thermodynamic criteria for stability, determination of stability based on electrochemical cell calculations allows an early introduction to the relative roles of the metal and the environment in corrosion. More than the usual emphasis is placed on the significance of environmental variables (pH, aeration, etc.), as is done throughout the text. Chapter 2 concludes with a rather detailed discussion of the so-called Pourbaix diagrams. While it is recognized that these diagrams must be used with caution in the analysis of corrosion problems, they are ready sources of information on the stability of metal/water systems and the corrosion products that can form. The somewhat more practical use of the diagrams is illustrated using Pourbaix's modified diagrams defining the conditions for immunity, passivity, and corrosion for several metals in aqueous environments.

Simple but pedagogically useful theories of electrode kinetics are presented in Chapter 3. This permits discussion of models for anodic and cathodic reactions at the metal/environment interface and for diffusion of species to and from the interface. Mathematical models of these theories lead to so-called kinetic parameters whose values govern the rate of the interface reaction. The range of values that these parameters can have and some of the variables that can influence the values are emphasized since these will relate to understanding the influence of such factors as surface conditions (roughness, corrosion product films, etc.), corrosion inhibitors and accelerators, and fluid velocity on corrosion rates. This chapter also introduces electrochemical measurements to determine values of the kinetic parameters.

The concepts in Chapters 2 and 3 are used in Chapter 4 to discuss the corrosion of so-called active metals. Chapter 5 continues with application to active/passive type alloys. Initial emphasis in Chapter 4 is placed on how the coupling of cathodic and anodic reactions establishes a mixed electrode or surface of corrosion cells. Emphasis is placed on how the corrosion rate is established by the kinetic parameters associated with both the anodic and cathodic reactions and by the physical variables such as anode/cathode area ratios, surface films, and fluid velocity. Polarization curves are used extensively to show how these variables determine the corrosion current density and corrosion potential and, conversely, to show how electrochemical measurements can provide information on the nature of a given corroding system. Polarization curves are also used to illustrate how corrosion rates are influenced by inhibitors, galvanic coupling, and external currents.

A separate chapter, Chapter 5, is used to introduce the corrosion behavior of active/passive type metals. This allows emphasis on the more complex anodic polarization behavior of these metals and the associated problems in interpreting their corrosion behavior. The chapter is introduced by discussing experimental observations on the anodic polarization of iron as a function of pH and how these observations can be related qualitatively to the iron-water Pourbaix diagram. Pedagogically, it would be desirable to analyze the corrosion behaviors of active/passive metals by relating their anodic polarization curves to curves for cathodic reactions as was done in Chapter 4 for nonpassive alloys. Because of the extreme sensitivity of an experimental curve to the environment, a reasonably complete curve usually can only be inferred. To do so requires understanding of the forms of experimental curves that can be derived from individual anodic and cathodic polarization curves. The basis for constructing such curves is discussed in some detail with ten cases analyzed showing the schematic construction of curves for an active/passive alloy with several environmental and alloy variables. The objective of the remainder of the chapter is to provide representative examples of (1) anodic polarization behaviors of commercial metals, (2) the effect of alloy composition on anodic polarization, and (3) the effect of several environmental variables on anodic polarization. Final sections illustrate the prediction of corrosion behavior of active/passive type alloys in specific environments.

Principles and procedures of electrochemical measurements used to investigate corrosion behavior are described in Chapter 6. Although some reference is made to subjects covered earlier in the book, the chapter is reasonably self contained and can be used as a condensed reference on electrochemical corrosion measurements and instrumentation. Also, the chapter is referenced in earlier chapters for readers wanting more information than accompanies an immediate discussion. Reference half cells and the use of electrometers for measuring electrochemical cell potentials are described in some detail including sources of error in measured values. This is followed by discussion of the potentiostat circuit and the use of potentiostats to determine the basic parameters of electrochemical reactions, and to measure corrosion potentials and current densities. Because of the more recent and expanding use of electrochemical impedance measurements to investigate many aspects of corrosion behavior, the theory and procedures underlying this technique are treated in some detail in the latter part of the chapter.

Chapter 7 describes localized corrosion phenomena and covers specific corrosion processes extending from pitting and crevice corrosion to stress corrosion cracking and corrosion fatigue. The discussion of each of these processes for several commercially important metals and alloys assumes familiarity with concepts covered in the earlier chapters. An objective of the chapter is to show that while there are general principles that can be brought to the investigation and understanding of corrosion behavior, identifying those that are applicable is frequently complicated because of conditions unique to each metal/environment system.

The material in Chapter 7 can be used in several ways: (1) it is a reasonably self-contained overview of localized corrosion and can be used as such for readers familiar with the principles developed in earlier chapters; (2) in covering the earlier chapters as a text, reference can be made to specific sections of Chapter 7 to illustrate the relevance of principles being developed to observations on real systems; (3) conversely, the chapter can be covered with emphasis on how knowledge of the principles of corrosion presented in earlier chapters is fundamental to understanding applied corrosion behavior; and (4) an outline of the major identifying features of each of the processes can be created as a guide to the reader in pursuing subjects for clarification or greater in-depth discussion.

The examples of localized corrosion in Chapter 7 are taken largely from the published literature, for which representative references are given. The major characteristics of each process are presented, followed by discussion of one or more mechanisms that have been proposed for the process. While generally a mechanism is discussed with reference to a specific metal and environment, application of the mechanism to other metal/environment systems should be recognized. The authors have used this chapter to emphasize that the range of corrosion phenomena directly involves a breadth of disciplines extending from electrochemistry and materials science to solid and fluid mechanics.

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