

Fundamentals of Electrochemical Corrosion

E.E. Stansbury

Professor Emeritus

Department of Materials Science and Engineering
The University of Tennessee

and

R.A. Buchanan

Robert M. Condra Professor

Department of Materials Science and Engineering
The University of Tennessee



**The Materials
Information Society**

ASM International®

Materials Park, Ohio 44073-0002

www.asminternational.org

Copyright © 2000
by
ASM International®
All rights reserved

No part of this book may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the written permission of the copyright owner.

First printing, July 2000

Great care is taken in the compilation and production of this book, but it should be made clear that NO WARRANTIES, EXPRESS OR IMPLIED, INCLUDING, WITHOUT LIMITATION, WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE, ARE GIVEN IN CONNECTION WITH THIS PUBLICATION. Although this information is believed to be accurate by ASM, ASM cannot guarantee that favorable results will be obtained from the use of this publication alone. This publication is intended for use by persons having technical skill, at their sole discretion and risk. Since the conditions of product or material use are outside of ASM's control, ASM assumes no liability or obligation in connection with any use of this information. No claim of any kind, whether as to products or information in this publication, and whether or not based on negligence, shall be greater in amount than the purchase price of this product or publication in respect of which damages are claimed. THE REMEDY HEREBY PROVIDED SHALL BE THE EXCLUSIVE AND SOLE REMEDY OF BUYER, AND IN NO EVENT SHALL EITHER PARTY BE LIABLE FOR SPECIAL, INDIRECT OR CONSEQUENTIAL DAMAGES WHETHER OR NOT CAUSED BY OR RESULTING FROM THE NEGLIGENCE OF SUCH PARTY. As with any material, evaluation of the material under end-use conditions prior to specification is essential. Therefore, specific testing under actual conditions is recommended.

Nothing contained in this book shall be construed as a grant of any right of manufacture, sale, use, or reproduction, in connection with any method, process, apparatus, product, composition, or system, whether or not covered by letters patent, copyright, or trademark, and nothing contained in this book shall be construed as a defense against any alleged infringement of letters patent, copyright, or trademark, or as a defense against liability for such infringement.

Comments, criticisms, and suggestions are invited, and should be forwarded to ASM International.

ASM International staff who worked on this project included Veronica Flint, Manager of Book Acquisitions; Scott Henry, Assistant Director, Reference Publications; Bonnie Sanders, Manager of Production; Carol Terman, Copy Editor; Kathleen Dragolich, Production Supervisor; and Alexandru Popaz-Pauna, Book Production Coordinator.

Library of Congress Cataloging-in-Publication Data

Stansbury, E.E.

Fundamentals of electrochemical corrosion / E.E. Stansbury and R.A. Buchanan
p. cm.

1. Electrolytic corrosion. 2. Corrosion and anti-corrosives. I. Buchanan, R.A. (Robert Angus), 1930-
II. Title.

TA462.S714 2000 620.1'1223—dc21 99-058428

ISBN: 0-87170-676-8

SAN: 204-7586

ASM International®

Materials Park, OH 44073-0002

www.asm-intl.org

Printed in the United States of America

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.

ASM International Technical Books Committee (1999-2000)

Sunniva R. Collins (Chair)
Swagelok/Nupro Company

Eugen Abramovici
Bombardier Aerospace (Canadair)

A.S. Brar
Seagate Technology Inc.

Ngai Mun Chow
Det Norske Veritas Pte Ltd.

Seetharama C. Deevi
Philip Morris, USA

Bradley J. Diak
Queen's University

Richard P. Gangloff
University of Virginia

Dov B. Goldman
Precision World Products

James F.R. Grochmal
Metallurgical Perspectives

Nguyen P. Hung
Nanyang Technological University

Serope Kalpakjian
Illinois Institute of Technology

Gordon Lippa
North Star Casteel

Jacques Masounave
Université du Québec

Charles A. Parker
AlliedSignal Aircraft Landing
Systems

K. Bhanu Sankara Rao
Indira Gandhi Centre for Atomic
Research

Mel M. Schwartz
Sikorsky Aircraft Corporation
(retired)

Peter F. Timmins
University College of the Fraser
Valley

George F. Vander Voort
Buehler Ltd.

Contents

Preface	xi
CHAPTER 1: Introduction and Overview of Electrochemical Corrosion	1
Definition and Examples of Corrosion	1
The Need to Control Corrosion	2
Corrosion Mechanisms	3
Electrochemical Corrosion Processes and Variables	5
Uniform Corrosion with pH as the Major Variable	5
Uniform Corrosion with pH and Dissolved Oxygen as Variables	6
Uniform Corrosion with Corrosion Product Formation	6
Some Basic Terminology, Reactions, and Variables in Aqueous Corrosion	8
The Elementary Electrochemical Corrosion Circuit	11
Criteria for Metal/Aqueous-Environment Reactions: Corrosion	14
Comments on Cathodic Reactions	14
Comments on Anodic Reactions	15
Corrosion Considerations Based on Relative Cathodic and Anodic Equilibrium Potentials	16
Importance of Solid Corrosion-Product Formation: Corrosion Acceleration Versus Passivation	18
Chapter 1 Review Questions	20
CHAPTER 2: Electrochemical Thermodynamics: The Gibbs Function, Electrochemical Reactions, and Equilibrium Potentials	23
Decrease in the Gibbs Function as a Condition for Spontaneous Reaction	23
Standard Gibbs Free-Energy Change for Chemical Reactions	26
Calculation of Standard Change of Gibbs Free Energy for Chemical Reactions from Gibbs Free Energy of Formation ..	27
Electrochemical Reactions, the Electrochemical Cell, and the Gibbs Free Energy Change	29
Interface Potential Difference and Half-Cell Potential	33

The Generalized Cell Reaction	37
The Nernst Equation: Effect of Concentration on Half-Cell Potential	42
Half-Cell Reactions and Nernst-Equation Calculations	45
Electrochemical Cell Calculations in Relationship to Corrosion	53
Graphical Representation of Electrochemical Equilibrium; Pourbaix Diagrams.....	60
Origin and Interpretation of Pourbaix Diagrams.....	60
Use of Pourbaix Diagrams to “Predict” Corrosion	67
Pourbaix Diagram Interpretations in Relationship to Corrosion	70
Chapter 2 Review Questions	79
Answers to Chapter 2 Review Questions	84
CHAPTER 3: Kinetics of Single Half-Cell Reactions.....	87
The Exchange Current Density	91
Charge-Transfer Polarization.....	98
Interpretation of Charge-Transfer Polarization from Experiment.....	104
Diffusion Polarization.....	108
Effect of Solution Velocity on Diffusion Polarization.....	113
Complete Polarization Curves for a Single Half-Cell Reaction	114
Polarization Behavior of the Hydrogen-Ion and Oxygen Reduction Reactions	116
Chapter 3 Review Questions	123
CHAPTER 4: Kinetics of Coupled Half-Cell Reactions.....	127
Relationship between Interface Potentials and Solution Potentials	129
A Simple Model of the Galvanically Coupled Electrode	133
A Physical Representation of the Electrochemical Behavior of Mixed Electrodes	141
Interpretation of E_{corr}	146
Faraday’s Law	147
Effects of Cathode-to-Anode Area Ratio	149
Interpretation of Experimental Polarization Curves for Mixed Electrodes	150
Summary of the Form and Source of Polarization Curves.....	159
Estimation of E_{corr} and I_{corr} for Iron as a Function of pH	160
Interpretation of Inhibitor Effects in Terms of Polarization Behavior	162

Galvanic Coupling	164
Case I: Galvanically Coupled Metals with Similar Electrochemical Parameters	165
Case II: Galvanic Coupling of a Metal to a Significantly More Noble Metal.	167
Cases III and IV: Galvanically Coupled Metals: One Metal Significantly Active	168
Cathodic Protection.	170
Cathodic Protection by Sacrificial Anodes	170
Cathodic Protection by Impressed Current	172
Cathodic Protection: Hydrogen Embrittlement	174
Example Calculations of Corrosion Potentials, Corrosion Currents, and Corrosion Rates for Aerated and Deaerated Environments, and the Effects of Galvanic Coupling	174
Chapter 4 Review Questions	178
Answers to Chapter 4 Review Questions	179
CHAPTER 5: Corrosion of Active-Passive Type Metals and Alloys.	183
Anodic Polarization Resulting in Passivity	183
Significance of the Pourbaix Diagram to Passivity	186
Experimental Observations on the Anodic Polarization of Iron	188
Relationship of Individual Anodic and Cathodic Polarization Curves to Experimentally Measured Curves.	193
Anodic Polarization of Several Active-Passive Metals.	202
Anodic Polarization of Iron	202
Effect of Crystal Lattice Orientation	203
Anodic Polarization of Aluminum	204
Anodic Polarization of Copper.	205
Anodic Polarization of Several Active-Passive Alloy Systems	206
Anodic Polarization Curves for Iron-Chromium Alloys	206
Anodic Polarization of Iron-Chromium-Molybdenum Alloys	207
Anodic Polarization of Iron-Chromium-Nickel Alloys	207
Anodic Polarization of Nickel-Chromium Alloys.	209
Anodic Polarization of Nickel-Molybdenum Alloys	210
Representative Polarization Behavior of Several Commercial Alloys	211
Additional Examples of the Influence of Environmental Variables on Anodic Polarization Behavior	214

Effects of Sulfide and Thiocyanate Ions on Polarization of Type 304 Stainless Steel	214
Effects of Chloride Ions	215
Polarization of Admiralty Brass	218
Effect of Temperature on the Polarization of Titanium	219
Prediction of Corrosion Behavior of Active-Passive Type Metals and Alloys in Specific Environments	220
Corrosion of Iron at pH = 7 in Deaerated and Aerated Environments and with Nitrite Additions	220
Corrosion of Iron, Nickel, Chromium, and Titanium in Sulfuric and Nitric Acids	222
Corrosion of Type 304 Stainless Steel in Sulfuric Acid	224
Chapter 5 Review Questions	227
Answers to Chapter 5 Review Questions	228
CHAPTER 6: Electrochemical Corrosion-Rate Measurements	233
Potential Measurement: Reference Electrodes and Electrometers (Ref 1)	239
The IR Correction to Experimentally Measured Potentials (Ref 2, 3)	243
Electrochemical Corrosion-Rate Measurement Methods and the Uniform-Corrosion Consideration	246
Tafel Analysis	248
Polarization Resistance (Ref 6–11)	251
Electrochemical Impedance Spectroscopy (EIS) (Ref 14–18)	254
Two-Electrode Method (Ref 19–20)	265
Reminder of the Uniform-Corrosion Consideration	266
Chapter 6 Review Questions	266
Answers to Chapter 6 Review Questions	268
CHAPTER 7: Localized Corrosion	271
The Concept of Localized Corrosion	271
Deviations from Strictly Uniform Corrosion	272
Surface Conditions Leading to Localized Corrosion	272
Environmental Conditions Leading to Localized Corrosion	272
Localized Corrosion Induced by Rupture of Otherwise Protective Coatings	273
Localized Corrosion due to Variations in Chemical Composition in Alloys	274
General Characterization of Pitting and Crevice Corrosion	275
Pitting of Typical Active-Passive Alloys	277

Pit Initiation	279
Pit Propagation	283
An Analysis of Pitting Corrosion in Terms of IR Potential Changes in Occluded Regions and Relationship to Polarization Curves	285
Surface Instabilities during Pit Initiation	289
Pit Initiation and the Critical Pitting Potential	293
Cyclic Anodic Polarization Scans: the Protection Potential	297
Investigations of Pitting Corrosion Using Chemical Environments	298
Effects of Temperature on Pitting: the Critical Pitting Temperature	301
Effect of Alloy Composition on Pitting	304
Effect of Fluid Velocity on Pitting	311
Effect of Surface Roughness and Oxides on Pitting of Stainless Steels	313
Pitting Corrosion of Carbon Steels	313
Corrosion Products and Surface Topology	314
Analysis of Pitting of Carbon Steels: Electrochemical Behavior	316
Pitting Corrosion of Copper	319
Analysis of Pitting of Copper with Reference to the Pourbaix Diagram	319
Variables in the Pitting of Copper	320
Mechanisms of Pitting of Copper	321
Pitting Corrosion of Aluminum	325
The Passive Film on Aluminum	325
Polarization Behavior of Aluminum	326
Mechanisms of Pitting Corrosion of Aluminum	327
Crevice Corrosion	328
General Description	328
The Critical Potential for Crevice Corrosion	330
Evaluation of Crevice Corrosion	332
Microbiologically Influenced Corrosion	333
Biofilms	333
Microorganisms and Effects on Solution Chemistry within Regions of the Biofilm	335
Ennoblement	337
Biocides	339
Intergranular Corrosion	340
Relationship of Alloy Microstructure to Susceptibility to Intergranular Corrosion	340
Intergranular Corrosion of Austenitic Stainless Steels	342
Intergranular Corrosion of Ferritic Stainless Steels	347

Intergranular Corrosion of Welded, Cast, and Duplex Stainless Steels	350
Intergranular Corrosion of Nickel-Base Alloys	350
Intergranular Corrosion of Aluminum-Base Alloys	353
Susceptibility of Stainless Steels to Intergranular Corrosion due to Welding	354
Measurement of Susceptibility of Stainless Steels to Intergranular Corrosion.	356
Environment-Sensitive Fracture	363
Characteristics of Environment-Sensitive Cracking	364
Evaluation of Susceptibility to Environment-Sensitive Cracking	366
Scope of Environment-Sensitive Fracture	368
Material/Environment Variables Affecting Crack Initiation and Growth	370
Mechanisms of Environment-Sensitive Crack Growth.	398
Application of Fracture Mechanics to the Evaluation of Environment-Sensitive Fracture.	406
APPENDIX: Selected Sources of Information: Corrosion Properties of Materials and Corrosion Testing	451

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 polar-

ization 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 ma-

For 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.

E.E. Stansbury
R.A. Buchanan



ASM International is the society for materials engineers and scientists, a worldwide network dedicated to advancing industry, technology, and applications of metals and materials.

ASM International, Materials Park, Ohio, USA
www.asminternational.org

This publication is copyright © ASM International®. All rights reserved.

Publication title	Product code
Fundamentals of Electrochemical Corrosion	#06594G

To order products from ASM International:

Online Visit www.asminternational.org/bookstore

Telephone 1-800-336-5152 (US) or 1-440-338-5151 (Outside US)

Fax 1-440-338-4634

Mail Customer Service, ASM International
9639 Kinsman Rd, Materials Park, Ohio 44073-0002, USA

Email CustomerService@asminternational.org

In Europe American Technical Publishers Ltd.
27-29 Knowl Piece, Wilbury Way, Hitchin Hertfordshire SG4 0SX,
United Kingdom
Telephone: 01462 437933 (account holders), 01462 431525 (credit card)
www.ameritech.co.uk

In Japan Neutrino Inc.
Takahashi Bldg., 44-3 Fuda 1-chome, Chofu-Shi, Tokyo 182 Japan
Telephone: 81 (0) 424 84 5550

Terms of Use. This publication is being made available in PDF format as a benefit to members and customers of ASM International. You may download and print a copy of this publication for your personal use only. Other use and distribution is prohibited without the express written permission of ASM International.

No warranties, express or implied, including, without limitation, warranties of merchantability or fitness for a particular purpose, are given in connection with this publication. Although this information is believed to be accurate by ASM, ASM cannot guarantee that favorable results will be obtained from the use of this publication alone. This publication is intended for use by persons having technical skill, at their sole discretion and risk. Since the conditions of product or material use are outside of ASM's control, ASM assumes no liability or obligation in connection with any use of this information. As with any material, evaluation of the material under end-use conditions prior to specification is essential. Therefore, specific testing under actual conditions is recommended.

Nothing contained in this publication shall be construed as a grant of any right of manufacture, sale, use, or reproduction, in connection with any method, process, apparatus, product, composition, or system, whether or not covered by letters patent, copyright, or trademark, and nothing contained in this publication shall be construed as a defense against any alleged infringement of letters patent, copyright, or trademark, or as a defense against liability for such infringement.