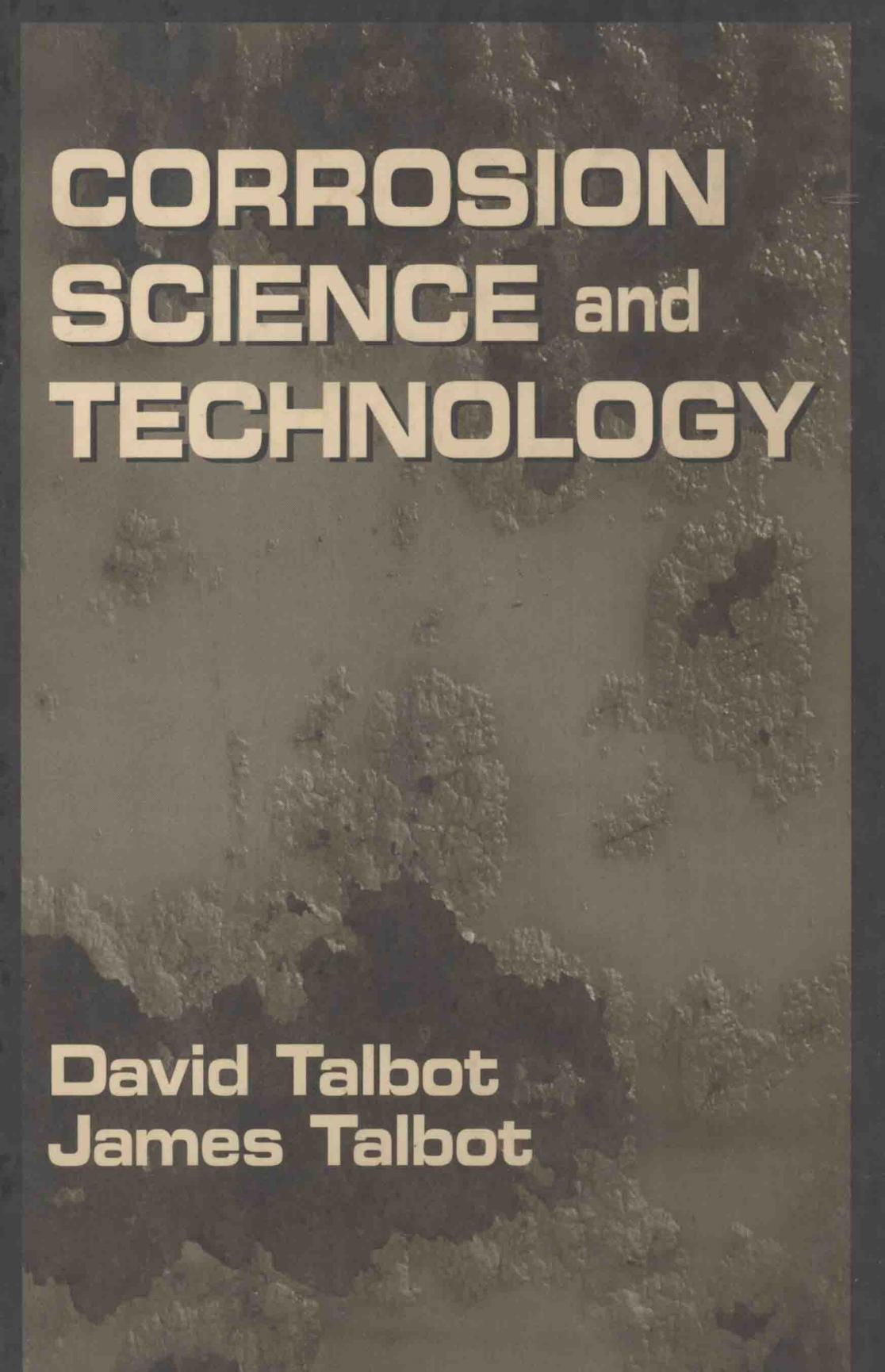


CORROSION SCIENCE and TECHNOLOGY



**David Talbot
James Talbot**

CORROSION SCIENCE and TECHNOLOGY

**David Talbot 藏书章
James Talbot**

江苏工业学院图书馆



CRC Press

Boca Raton Boston New York Washington London

Library of Congress Cataloging-in-Publication Data

Talbot, David

Corrosion science and technology/ David Talbot and James Talbot
p. cm. (CRC series in materials science and technology)

Includes bibliographical references and index.

ISBN 0-8493-8224-6

1. Chemical engineering—materials science. 2. Mechanical engineering—materials
science. I. Talbot, James. II. Title. III. Series.

H749.H34B78 1997

616'.0149—dc20

for Library of Congress

97-57109
CIP

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage or retrieval system, without prior permission in writing from the publisher.

The consent of CRC Press LLC does not extend to copying for general distribution, for promotion, for creating new works, or for resale. Specific permission must be obtained in writing from CRC Press LLC for such copying.

Direct all inquiries to CRC Press LLC, 2000 Corporate Blvd., N.W., Boca Raton, Florida 33431.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation, without intent to infringe.

© 1998 by CRC Press LLC

No claim to original U.S. Government works

International Standard Book Number 0-8493-8224-6

Library of Congress Card Number 97-57109

Printed in the United States of America 1 2 3 4 5 6 7 8 9 0

Printed on acid-free paper

CORROSION SCIENCE and TECHNOLOGY

CRC Series in
Materials Science and Technology

Series Editor
Brian Ralph

**Control of Microstructures and Properties
in Steel Arc Welds**
Lars-Erik Svensson

The Extraction and Refining of Metals
Colin Bodsworth

**The Quantitative Description of the
Microstructure of Materials**
K.J. Kurzydłowski and Brian Ralph

**Grain Growth and Control of Microstructure
and Texture in Polycrystalline Materials**
Vladimir Novikov

Corrosion Science and Technology
D. E. J. Talbot and J. D. R. Talbot

Preface

Engineering metals are unstable in natural and industrial environments. In the long term, they inevitably revert to stable chemical species akin to the chemically combined forms from which they are extracted. In that sense, metals are only borrowed from nature for a limited time. Nevertheless, if we understand their interactions with the environments to which they are subjected and take appropriate precautions, degradation can be arrested or suppressed long enough for them to serve the purposes required. The measures that are taken to prolong the lives of metallic structures and artifacts must be compatible with other requirements, such as strength, density, thermal transfer, and wear resistance. They must also suit production arrangements and be proportionate to the expected return on investment. Thus, problems related to corrosion and its control arise within technologies, but solutions often depend on the application of aspects of chemistry, electrochemistry, physics, and metallurgy that are not always within the purview of those who initially confront the problems.

Corrosion is the transformation of metallic structures into other chemical structures, most often through the intermediary of a third structure, i.e., water and a first task is to characterize these structures and examine how they determine the sequences of events that result in metal wastage. These matters are the subjects of Chapters 2, 3, 4, and 5. The information is applied in Chapter 6 to examine the options available for the most usual strategy to control corrosion, the application of protective coatings. Chapters 7 through 9 examine the attributes and corrosion behavior of three groups of metallic materials, plain carbon steels and irons, stainless steels, and aluminum alloys.

The final chapters deal with some practical implications. Corrosion control is only one aspect of the technologies within which it is exercised and the approaches adopted must accommodate other requirements in the most economic way. For this reason, some total technologies are selected to illustrate how the approach to corrosion control is conditioned by their particular circumstances. Aviation is a capital intensive industry in which the imperatives are flight safety, the protection of investment and uninterrupted operation of aircraft over a long design life. In automobile manufacture, the design life is less but retail sales potential through positive customer perception is vitally important. Food handling introduces aspects of public health, biological contributions to corrosion problems, and the mass production of food cans that are low-value corrosion-resistant artifacts. Building construction has a menu of different approaches to

corrosion control from which solutions are selected to suit client requirements, local government ordinances and changing patterns of business under the pressures of competitive tendering.

The form of the present text has evolved from long experience of lectures and seminars arranged for students and graduates drawn into corrosion-related work from a wide variety of different backgrounds.

The Authors

David Talbot graduated with B.Sc. and M.Sc. from the University of Wales and Ph.D. from Brunel University for research on gas-metal equilibria. From 1949 to 1966 he was employed at the Research Laboratories of the British Aluminium Company Ltd., contributing to research promoting the development of manufacturing processes and to customer service. From 1966 to 1994 he taught courses on corrosion and other aspects of chemical metallurgy at Brunel University, maintaining an active interest in research and development, mainly in collaboration with manufacturing industries in the U.K. and U.S.A. He is a member of the Institute of Materials with Chartered Engineer status and has served as a member of Council of the London Metallurgical Society. He has written many papers on chemical aspects of metallurgy, a review on metal-hydrogen systems in *International Metallurgical Reviews* and a section on gas-metal systems in *Smithells Metals Reference Book*.

James Talbot graduated with B.Sc., ARCS from Imperial College, London, M.Sc. from Brunel University and Ph.D. from the University of Reading for research on the physical chemistry of aqueous solutions and its application to natural waters. He is currently employed at the River Laboratory of the Institute of Freshwater Ecology, East Stoke, Wareham, Dorset, U.K. to assess and predict physical chemical changes that occur in river management. He has written papers on the speciation of solutes in natural waters.

Acknowledgments

The authors wish to acknowledge their gratitude to Professor Brian Ralph and Professor Colin Bodsworth for their interest, encouragement, and valuable suggestions.

They also wish to thank the following people for the courtesy of their expert advice:

Mr. Mick Morris, Manager, Aircraft Structures, British Airways — Corrosion control in airframes.

Mr. David Bettridge, Rolls-Royce Limited — Corrosion prevention in gas turbine engines.

Mr. Alan Turrell and Mr. John Creese, The Rover Group — Corrosion protection for automobiles.

Mr. Ray Cox, U. K. Building Research Establishment — Corrosion control in building.

Mr. Derek Bradshaw, Alpha Anodizing Ltd. — Surface cleaning and chromate treatment of aluminum alloys.

Mr. Alan Mudie, Guinness Brewery — Corrosion control in brewing.

Contents

Preface.....	xii
1 Overview of Corrosion and Protection Strategies	1
1.1 Corrosion in Aqueous Media.....	1
1.1.1 Corrosion as a System Characteristic.....	1
1.1.2 The Electrochemical Origin of Corrosion.....	2
1.1.3 Stimulated Local Corrosion.....	3
1.2 Thermal Oxidation	4
1.2.1 Protective Oxides	4
1.2.2 Non-Protective Oxides.....	5
1.3 Environmentally Sensitive Cracking.....	5
1.4 Strategies for Corrosion Control.....	5
1.4.1 Passivity.....	5
1.4.2 Conditions in the Environment.....	6
1.4.3 Cathodic Protection.....	6
1.4.4 Protective Coatings	7
1.4.5 Corrosion Costs	7
1.4.6 Criteria for Corrosion Failure.....	7
1.4.7 Material Selection.....	8
1.4.8 Geometric Factors	10
1.5 Some Symbols, Conventions, and Equations	10
1.5.1 Ions and Ionic Equations	10
1.5.2 Partial Reactions.....	11
1.5.3 Representation of Corrosion Processes	12
2 Structures Concerned in Corrosion Processes	15
2.1 Origins and Characteristics of Structure.....	15
2.1.1 Phases	15
2.1.2 The Role of Electrons in Bonding.....	21
2.1.3 The Concept of Activity	26
2.2 The Structure of Water and Aqueous Solutions.....	27
2.2.1 The Nature of Water.....	27
2.2.2 The Water Molecule	28
2.2.3 Liquid Water.....	28
2.2.4 Autodissociation and pH of Aqueous Solutions	31
2.2.5 The pH Scale.....	32
2.2.6 Foreign Ions in Solution.....	33

2.2.7	Ion Mobility	35
2.2.8	Structure of Water and Ionic Solutions at Metal Surfaces	36
2.2.9	Constitutions of Hard and Soft Natural Waters	38
2.3	The Structures of Metal Oxides	43
2.3.1	Electronegativity	44
2.3.2	Partial Ionic Character of Metal Oxides.....	45
2.3.3	Oxide Crystal Structures.....	46
2.3.4	Conduction and Valence Electron Energy Bands.....	49
2.3.5	The Origins of Lattice Defects in Metal Oxides	50
2.3.6	Classification of Oxides by Defect Type	55
2.4	The Structures of Metals	59
2.4.1	The Metallic Bond	60
2.4.2	Crystal Structures and Lattice Defects.....	61
2.4.3	Phase Equilibria	61
2.4.4	Structural Artifacts Introduced During Manufacture	67
3	Thermodynamics and Kinetics of Corrosion Processes.....	71
3.1	Thermodynamics of Aqueous Corrosion	71
3.1.1	Oxidation and Reduction Processes in Aqueous Solution.....	71
3.1.2	Equilibria at Electrodes and the Nernst Equation	74
3.1.3	Standard State for Activities of Ions in Solution	75
3.1.4	Electrode Potentials	76
3.1.5	Pourbaix (Potential-pH) Diagrams	80
3.2	Kinetics of Aqueous Corrosion.....	95
3.2.1	Kinetic View of Equilibrium at an Electrode	96
3.2.2.	Polarization	97
3.2.3	Polarization Characteristics and Corrosion Velocities	105
3.2.4	Passivity.....	110
3.2.5	Breakdown of Passivity	113
3.2.6	Corrosion Inhibitors.....	115
3.3	Thermodynamics and Kinetics of Dry Oxidation.....	119
3.3.1	Factors Promoting the Formation of Protective Oxides	119
3.3.2	Thin Films and the Cabrera-Mott Theory	120
3.3.3	Thick Films, Thermal Activation and the Wagner Theory.....	121

3.3.4	Selective Oxidation of Components in an Alloy	129
	Sample Problems and Solutions	136
	Appendix: Construction of Some Pourbaix Diagrams	144
4	Mixed Metal Systems and Cathodic Protection.....	155
4.1	Galvanic Stimulation.....	155
4.1.1	Bimetallic Couples	156
4.1.2	The Origin of the Bimetallic Effect.....	156
4.1.3	Design Implications	157
4.2	Protection by Sacrificial Anodes	163
4.2.1	Principle.....	163
4.2.2	Application	164
4.3	Cathodic Protection by Impressed Current	165
5	The Intervention of Stress.....	169
5.1	Stress-Corrosion Cracking (SCC).....	169
5.1.1	Characteristic Features	171
5.1.2	Stress-Corrosion Cracking in Aluminum Alloys	171
5.1.3	Stress-Corrosion Cracking in Stainless Steels	174
5.1.4	Stress-Corrosion Cracking in Plain Carbon Steels.....	176
5.2	Corrosion Fatigue	177
5.2.1	Characteristic Features	179
5.2.2	Mechanisms	179
5.3	Erosion-Corrosion and Cavitation.....	180
5.3.1	Erosion-Corrosion	180
5.3.2	Cavitation	180
5.4	Precautions Against Stress-Induced Failures.....	181
6	Protective Coatings.....	185
6.1	Surface Preparation	185
6.1.1	Surface Conditions of Manufactured Metal Forms	185
6.1.2	Cleaning and Preparation of Metal Surfaces	187
6.2	Electrodeposition	193
6.2.1	Application and Principles	193
6.2.2	Electrodeposition of Nickel	198
6.2.3	Electrodeposition of Copper.....	201
6.2.4	Electrodeposition of Chromium	201
6.2.5	Electrodeposition of Tin.....	204

6.3	Hot-Dip Coatings	208
6.3.1	Zinc Coatings (Galvanizing).....	208
6.3.2	Tin coatings	209
6.3.3	Aluminum Coatings.....	209
6.4	Conversion Coatings	210
6.4.1	Phosphating.....	210
6.4.2	Anodizing	212
6.4.3	Chromating.....	216
6.5	Paint Coatings for Metals.....	219
6.5.1	Paint Components	220
6.5.2	Application	224
6.5.3	Paint Formulation	225
6.5.4	Protection of Metals by Paint Systems.....	226
7	Corrosion of Iron and Steels	227
7.1	Microstructures of Irons and Steels	227
7.1.1	Solid Solutions in Iron	227
7.1.2	The Iron-Carbon System	229
7.1.3	Plain Carbon Steels	230
7.1.4	Cast Irons.....	232
7.2	Rusting	234
7.2.1	Species in the Iron-Oxygen-Water System.....	234
7.2.2	Rusting in Aerated Water	236
7.2.3	Rusting in Air	239
7.2.4	Rusting of Cast Irons.....	241
7.3	The Oxidation of Iron and Steels	243
7.3.1	Oxide Types and Structures.....	243
7.3.2	Phase Equilibria in the Iron–Oxygen System.....	243
7.3.3	Oxidation Characteristics	245
7.3.4	Oxidation of Steels	247
7.3.5	Oxidation and Growth of Cast Irons.....	249
8	Stainless Steels	253
8.1	Phase Equilibria.....	254
8.1.1	The Iron-Chromium System	254
8.1.2	Effects of Other Elements on the Iron-Chromium System	255
8.1.3	Schaeffler Diagrams	258
8.2	Commercial Stainless Steels.....	260
8.2.1	Classification	260
8.2.2	Structures.....	260
8.3	Resistance to Aqueous Corrosion	263
8.3.1	Evaluation from Polarization Characteristics	263

8.3.2	Corrosion Characteristics	270
8.4	Resistance to Dry Oxidation	277
8.5	Applications.....	279
8.5.1	Ferritic Steels	279
8.5.2	Austenitic Steels.....	279
8.5.3	Hardenable Steels.....	281
8.5.4	Duplex Steels	281
8.5.5	Oxidation-Resistant Steels	281
	Problems and Solutions	283
9	Corrosion Resistance of Aluminum and Its Alloys	287
9.1	Summary of Physical Metallurgy of Some Standard Alloys	287
9.1.1	Alloys Used Without Heat Treatment.....	288
9.1.2	Heat Treatable (Aging) Alloys.....	291
9.1.3	Casting Alloys	294
9.2	Corrosion Resistance	294
9.2.1	The Aluminum-Oxygen-Water System	295
9.2.2	Corrosion Resistance of Pure Aluminum in Aqueous Media	297
9.2.3	Corrosion Resistance of Aluminum Alloys in Aqueous Media	300
9.2.4	Corrosion Resistance of Aluminum and its Alloys in Air	304
9.2.5	Geometric Effects	305
10	Corrosion and Corrosion Control in Aviation.....	309
10.1	Airframes	310
10.1.1	Materials of Construction	310
10.1.2	Protective Coatings	310
10.1.3	Corrosion of Aluminum Alloys in Airframes.....	310
10.1.4	External Corrosion	311
10.1.5	Systematic Assessment for Corrosion Control	312
10.1.6	Environmentally Sensitive Cracking.....	313
10.2	Gas Turbine Engines.....	314
10.2.1	Engine Operation	314
10.2.2	Brief Review of Nickel Superalloys.....	316
10.2.3	Corrosion Resistance.....	317
10.2.4	Engine Environment	319
10.2.5	Materials	321
10.2.6	Monitoring and Technical Development	324
11	Corrosion Control in Automobile Manufacture.....	327
11.1	Overview.....	327

11.2	Corrosion Protection for Automobile Bodies.....	327
11.2.1	Design Considerations	327
11.2.2	Overview of Paint-Shop Operations	329
11.2.3	Cleaning and Pretreatment of Body Shells	330
11.2.4	Phosphating.....	330
11.2.5	Application of Paint.....	333
11.2.6	Whole-Body Testing	334
11.3	Corrosion Protection for Engines	334
11.3.1	Exhaust Systems.....	334
11.3.2	Cooling Systems	335
11.3.3	Moving Parts	336
11.4	Bright Trim.....	337
11.4.1	Electrodeposited Nickel Chromium Systems	337
11.4.2	Anodized Aluminum	338
12	Control of Corrosion in Food Processing and Distribution	339
12.1	General Considerations	339
12.1.1	Public Health.....	339
12.1.2	Food Product Environments.....	341
12.2	The Application of Tinplate for Food and Beverage Cans	344
12.2.1	Historical	344
12.2.2	Modern Tinplate Cans.....	344
12.2.3	Steel Base for Tinplate Manufacture	346
12.2.4	The Manufacture of Tinplate	347
12.2.5	Tin-Free Steel for Packaging	351
12.3	Dairy Industries.....	352
12.3.1	Milk and Its Derivatives	352
12.3.2	Materials Used in the Dairy Industry	355
12.4	Brewing	356
12.4.1	The Brewing Process	356
12.4.2	Materials Used for Brewing Plant	359
12.4.3	Beer Barrels, Casks, and Kegs	361
13	Control of Corrosion in Building Construction	365
13.1	Introduction	365
13.2	Structures	366
13.2.1	Steel Bar for Reinforced Concrete Frames	366
13.2.2	Steel Frames.....	371
13.2.3	Traditional Structures	372
13.3	Cladding	373
13.3.1	Reinforced Concrete Panels	373
13.3.2	Aluminum Alloy Panels.....	373
13.4	Metal Roofs, Siding, and Flashing.....	374

13.4.1	Self-Supporting Roofs and Siding.....	374
13.4.2	Fully Supported Roofs and Flashings.....	375
13.5	Plumbing and Central Heating Installations	376
13.5.1	Pipes.....	376
13.5.2	Tanks	377
13.5.3	Joints	377
13.5.4	Central-Heating Circuits.....	377
13.6	Corrosion of Metals in Timber	378
13.6.1	Contact Corrosion	378
13.6.2	Corrosion by Vapors from Wood.....	379
13.7	Application of Stainless Steels in Leisure Pool Buildings.....	380
13.7.1	Corrosion Damage	380
13.7.2	Control	381
Index		383

1

Overview of Corrosion and Protection Strategies

Metals in service often give a superficial impression of permanence, but all except gold are chemically unstable in air and air-saturated water at ambient temperatures and most are also unstable in air-free water. Hence almost all of the environments in which metals serve are potentially hostile and their successful use in engineering and commercial applications depends on protective mechanisms. In some metal/environment systems the metal is protected by passivity, a naturally formed surface condition inhibiting reaction. In other systems the metal surface remains active and some form of protection must be provided by design; this applies particularly to plain carbon and low-alloy irons and steels, which are the most prolific, least expensive, and most versatile metallic materials. Corrosion occurs when protective mechanisms have been overlooked, break down, or have been exhausted, leaving the metal vulnerable to attack.

Practical corrosion-related problems are often discovered in the context of engineering and allied disciplines, where the approach may be hindered by unfamiliarity with the particular blend of electrochemistry, metallurgy, and physics which must be brought to bear if satisfactory solutions are to be found. This brief overview is given to indicate the relevance of these various disciplines and some relationships between them. They are described in detail in subsequent chapters.

1.1 Corrosion in Aqueous Media

1.1.1 Corrosion as a System Characteristic

Some features of the performance expected from metals and metal artifacts in service can be predicted from their intrinsic characteristics assessed from their compositions, structures as viewed in the microscope, and past history of thermal and mechanical treatments they may have