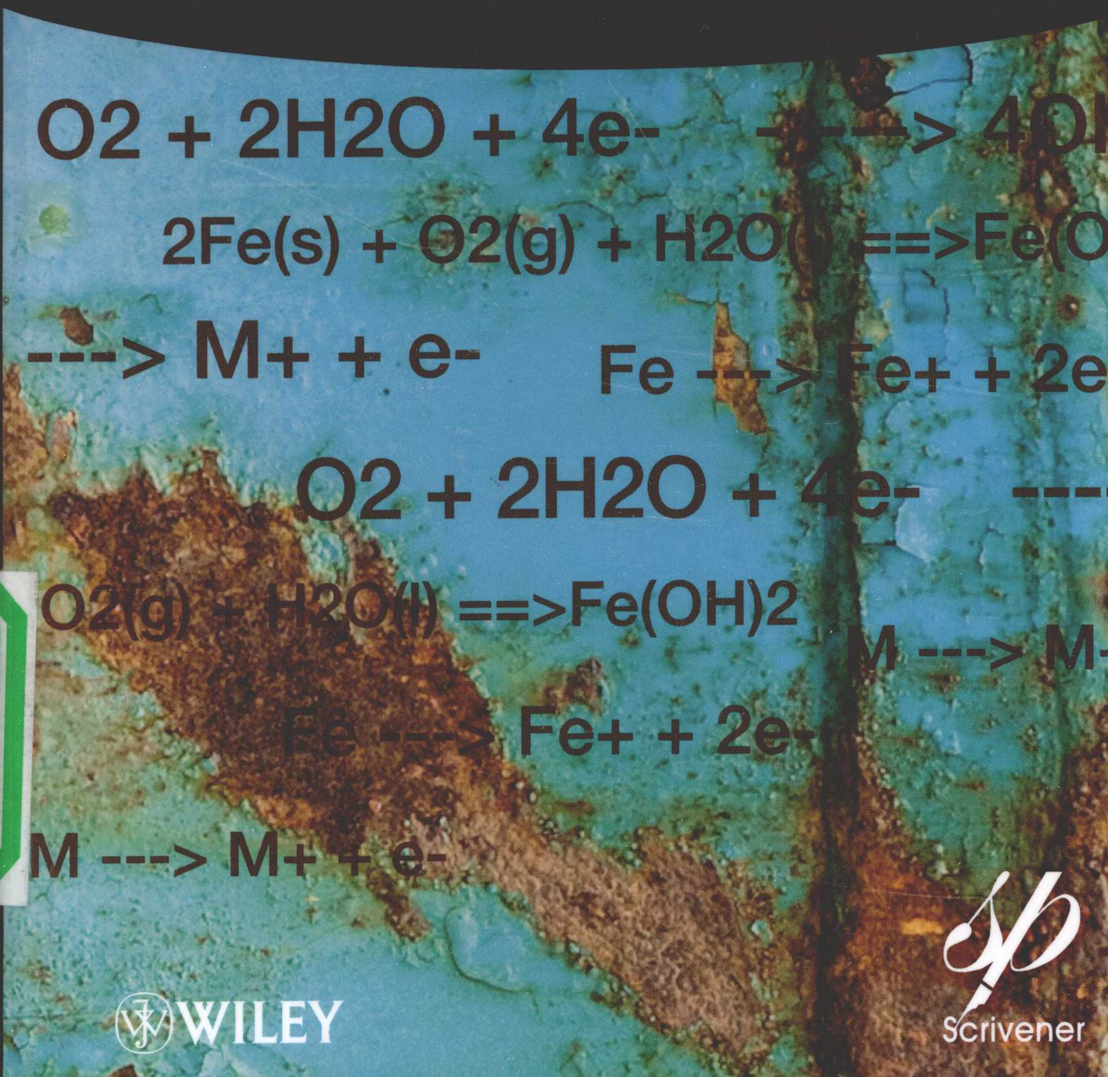
Volkan Cicek and Bayan Al-Numan

CORROSION CHEMISTRY



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Scrivener

WILEY

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

ISBN 978-0-470-94307-6

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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Scrivener Publishing
3 Winter Street, Suite 3
Salem, MA 01970

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Acknowledgements

First of all, I would like to express my sincere appreciation and gratefulness to Wiley-Scrivener Publications since they were eager to fund such a project at a time, when almost all academic publications in Iraq ceased. We all hope that the negative situation in Iraq is temporary and Iraq will take its place in the academic world in the near future once more.

I also would like to acknowledge Dr. Bayan Al Numan for contributing to this book with a vast chapter "Corrosion in Engineering Materials," and graphic artist Khabbab Habib for his support when needed.

I also would like to acknowledge my Ph.D. advisor, Dr. Allen W. Apblett, for his guidance, motivation, and inspiration throughout my Ph.D. education. His valuable advice, criticism, and encouragement have greatly helped me. I have benefited much from his broad range of knowledge, and his scientific approach.

Thanks are also due to my father, my mom, my sister, my relatives, and friends for their moral support, and encouragement throughout the years.

Finally, I am deeply indebted to my wife, Mine Cicek, for her unconditional love, patience, care, and sacrifice. Your moral support during this time, together with the enthusiasm that I got from our two lovely children, Furkan and Zehra, was invaluable to me.

Preface

This book was written and published as a reference for engineers and a textbook for students, due to the necessity of such a book in the area of corrosion chemistry and corrosion science in general.

Corrosion is, in essence, a chemical process, and it is crucial to understand the dynamics from a chemical perspective before proceeding with analyses, designs and solutions from engineering aspect. The opposite is also true in the sense that scientists should take into consideration the contemporary aspects of the issue as it relates to the daily life before proceeding with specifically designed theoretical solutions. Thus, this book is advised to both theoreticians and practitioners of corrosion alike.

Corrosion costs billions of dollars to each and every single economy in the world however is only taught in the form of a single semester elective course and that is sometimes at undergraduate level since most probably it is a joint discipline that is associated with many others, thus does not belong to any major science altogether. Corrosion is associated primarily with major engineering sciences such as chemical engineering, civil engineering, petroleum engineering, mechanical engineering, metallurgical engineering, mining engineering among others and major fundamental sciences such as subdisciplines of physical, inorganic and analytical chemistry as well as physics and biology, e.g., electrochemistry, surface chemistry and physics, solution chemistry, crystalline and amorphous structures and solid state chemistry and physics in general, microbiology, etc.

Hence, a reference book that summarizes the process with its contemporary aspects with respect to both scientific and engineering aspects was needed. Additionally, being such a joint discipline such a book should not overwhelm the reader with too much detail but only enough to understand the process as this was aimed in this book.

In addition to be used as a reference, this book could be used as a textbook most conveniently for a single semester elective course; however, the period of the course could be adjusted to fit into a long or a short summer term as well as a complete year depending on the course. In the case that this book is used as a textbook for a full year course, using supplementary resources may be beneficial especially in the case of engineering sciences.

Contents

1

Corrosion and Its Definition

According to American Society for Testing and Materials' corrosion glossary, corrosion is defined as "the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties".[1]

Other definitions include Fontana's description that corrosion is the extractive metallurgy in reverse,[2] which is expected since metals thermodynamically are less stable in their elemental forms than in their compound forms as ores. Fontana states that it is not possible to reverse fundamental laws of thermodynamics to avoid corrosion process; however, he also states that much can be done to reduce its rate to acceptable levels as long as it is done in an environmentally safe and cost-effective manner.

In today's world, a stronger demand for corrosion knowledge arises due to several reasons. Among them, the application of new materials requires extensive information concerning corrosion behavior of these particular materials. Also the corrosivity of water and atmosphere have increased due to pollution and acidification caused by industrial production. The trend in technology to produce stronger materials with decreasing size makes it relatively more expensive to add a corrosion allowance to thickness. Particularly in applications where accurate dimensions are required, widespread use of welding due to developing construction sector has increased the number of corrosion problems.[3] Developments in other sectors such as offshore oil and gas extraction, nuclear power production and medicinal health have also required stricter rules and control. More specifically, reduced allowance of chromate-based corrosion inhibitors due to their toxicity constitutes one of the major motivations to replace chromate inhibitors with environmentally benign and efficient ones.

2

The Corrosion Process and Affecting Factors

There are four basic requirements for corrosion to occur. Among them is the anode, where dissolution of metal occurs, generating metal ions and electrons. These electrons generated at the anode travel to the cathode via an electronic path through the metal, and eventually they are used up at the cathode for the reduction of positively charged ions. These positively charged ions move from the anode to the cathode by an ionic current path. Thus, the current flows from the anode to the cathode by an ionic current path and from the cathode to the anode by an electronic path, thereby completing the associated electrical circuit. Anode and cathode reactions occur simultaneously and at the same rate for this electrical circuit to function.[4] The rate of anode and cathode reactions (that is the corrosion rate), is defined by American Society for Testing and Materials as material loss per area unit and time unit.[1]

In addition to the four essentials for corrosion to occur, there are secondary factors affecting the outcome of the corrosion reaction. Among them there are temperature, pH, associated fluid dynamics, concentrations of dissolved oxygen and dissolved salt. Based on pH of the media, for instance, several different cathodic reactions are possible. The most common ones are:

Hydrogen evolution in acid solutions,

$$2H^{+}2e^{-} \longrightarrow H_2 \tag{2.1}$$

Oxygen reduction in acid solutions,

$$O_2 + 4H^{+}4e^{-} \longrightarrow 2H_2O \tag{2.2}$$

Hydrogen evolution in neutral or basic solutions,

$$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-} \tag{2.3}$$

Oxygen reduction in neutral or basic solutions,

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \tag{2.4}$$

The metal oxidation is also a complex process and includes hydration of resulted metal cations among other subsequent reactions.

$$M^{0} \longrightarrow M^{n+} + ne^{-}, \tag{2.5}$$

In terms of pH conditions, this book has emphasized near neutral conditions as the media leading to less emphasis on hydrogen evolution and oxygen reduction reactions, since both hydrogen evolution and oxygen reduction reactions that take place in acidic conditions are less common.

Among cathode reactions in neutral or basic solutions, oxygen reduction is the primary cathodic reaction due to the difference in electrode potentials. Thus, oxygen supply to the system, in which corrosion takes place, is of utmost importance for the outcome of corrosion reaction. Inhibitors are commonly tested in stagnant solutions for the purpose of weight-loss tests, thus ruling out the effects of varying fluid dynamics on corrosion. Weight-loss tests are performed at ambient conditions, thus effects of temperature and dissolved oxygen amounts are not tested as well, while for salt fog chamber tests, temperature is varied for accelerated corrosion testing. For both weight loss tests and salt fog chamber tests, however, dissolved salt concentrations are commonly kept high for accelerated testing to be possible.

When corrosion products such as hydroxides are deposited on a metal surface, a reduction in oxygen supply occurs, since the oxygen has to diffuse through deposits. Since the rate of metal dissolution is equal to the rate of oxygen reduction, a limited supply and limited reduction rate of oxygen will also reduce the corrosion rate. In this case the corrosion is said to be under cathodic control.[5] In other cases corrosion products form a dense and continuous surface film of oxide closely related to the crystalline structure of metal. Films of this type prevent primarily the conduction of metal ions from metal-oxide interface to the oxide-liquid interface, resulting in a corrosion reaction that is under anodic control.[5] When this happens, passivation occurs and metal is referred as a passivated metal. Passivation is typical for stainless steels and aluminum.