

**HANDBOOK
ON
CORROSION
TESTING
AND
EVALUATION**

Edited by
William H. Ailor

HANDBOOK ON CORROSION TESTING AND EVALUATION

Edited by

W. H. AILOR

Reynolds Metals Company
Richmond, Virginia



Sponsored by

THE ELECTROCHEMICAL SOCIETY, INC. Princeton, New Jersey

John Wiley and Sons, Inc. New York · London · Sydney · Toronto

Copyright © 1971, by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

No part of this book may be reproduced by any means, nor transmitted, nor translated into a machine language without the written permission of the publishers.

Library of Congress Catalog Card Number: 74-162423

ISBN 0-471-00985-7

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

THE CORROSION MONOGRAPH SERIES

R. T. Foley, N. Hackerman, C. V. King, F. L. LaQue, and Z. A. Forouli, Editors

Kofstad, *High-Temperature Oxidation of Metals*

Logan, *The Stress Corrosion of Metals*

Godard, Jepson, Bothwell, and Kane, *The Corrosion of Light Metals*

Leidheiser, *The Corrosion of Co, per, Tin, and Their Alloys*

Berry, *Corrosion in Nuclear Applications*

Ailor, *Handbook on Corrosion Testing and Evaluation*

In Preparation (Titles Tentative)

Forouli, *Aqueous Corrosion and Its Inhibition*

LaQue, *Marine Corrosion*

Coburn, *Atmospheric Corrosion*

Friend, *Corrosion of Nickel and Nickel Base Alloys*

Myers and Greene, *Potentiostatic Anodic Polarization*

PREFACE TO THE SERIES

The *Corrosion Monograph Series* is the mechanism chosen by the Corrosion Division of The Electrochemical Society to bring the corrosion literature up to date.

Since 1945, the field of corrosion has seen a tremendous amount of research and development stimulated by problems related to great advances in technology and facilitated by parallel advances in corrosion science. This has resulted in a corresponding expansion in the published literature. Indeed, in the late forties whole subdivisions of corrosion knowledge, such as that related to corrosion of titanium and to corrosion by ultra pure water at high temperature, were practically nonexistent.

Although knowledge in some areas of corrosion has continued to evolve at a less accelerated pace, data published in the mid-forties have been supplemented and supported by results of continuing studies that have provided an enlarged base for dealing with specific problems.

As a result of the appearance of numerous new concepts and such a large body of new data in so many areas, the total mass of information has become more than a single-volume treatise can contain. The preparation of monographs in selected areas, to be followed by appropriate revision, was chosen as the preferred course to keep pace with hoped-for progress.

These monographs are being written by specialists in each field, and the number of authors contributing to a single volume has been intentionally kept small to provide for such sharpening of point of view as is offered by small areas, but not large ones. Also, this accelerates publication.

The nature of the presentation, that is, the relative emphasis on the scientific aspects as contrasted to the engineering aspects, varies with the subject being dealt with, the nature of pertinent data, and the response of

the authors to these influences. The several volumes include critical exposition of modern theories as well as specific data of the handbook type so useful to the practicing engineer. With this approach, the Series is designed to be useful to basic scientists working in research as well as to engineers confronted with corrosion problems in the field.

The Corrosion Monograph Series Committee

R. T. Foley, Chairman

N. Hackerman

C. V. King

F. L. LaQue

Z. A. Foroulis

PREFACE

Corrosion is a process contributing to economic losses and pollution of our environment. This degradation of metals and their alloys occurs in man-made as well as natural environments. Methods of corrosion control become more and more important as we are increasingly concerned about conserving our natural resources. For effective control of corrosion, we must have a thorough understanding of its nature and methods of measurement.

In 1967 the Electrochemical Society proposed that the subject "*Corrosion Testing*" be included in its current Corrosion Monograph Series. It was further planned that the book would be developed around invited and offered contributions from recognized specialists in the field of corrosion testing. The papers would be edited to give a unified contemporary and authoritative volume on corrosion testing.

With these thoughts in mind, I arranged a Symposium on the State of the Art in Corrosion Testing for the June 1970 American Society for Testing and Materials Annual Meeting in Toronto, Ontario, Canada. The symposium was under the joint sponsorship of the Electrochemical Society, the American Society for Testing and Materials, and the National Association of Corrosion Engineers. At the four-day symposium a series of thirty-three papers were presented. These papers comprehensively treated the many facets of corrosion testing.

This handbook, a record of the conference, is dedicated to an in-depth study by scientists and engineers of methods used for corrosion testing. It should give insight into the current thinking and methods used by corrosion workers in many fields. The practical problems and theoretical aspects of corrosion testing are discussed. Metallurgical considerations, effects of

environments and temperature, and methods of corrosion evaluation are included. Laboratory methods are compared and contrasted with field and in-service testing procedures. The interpretation of corrosion test results and the significance of these results are considered.

The usefulness of this edition, then, will be due for the most part to the conscientious efforts of the contributing authors. Any errors or inaccuracies are of course my responsibility. A proper treatment of the subject requires a balance of emphasis regarding the fundamental and practical aspects of corrosion testing. An objective for this volume has been that it contain material that is both timely and timeless—that it help to build the future from the experience of the past. If this book meets the needs of the practicing corrosion engineer and the research scientist, it will have served its purpose. If it finds a useful place on the corrosion bookshelf, its objectives will have been met.

Richmond, Virginia
March 1971

W. H. AILOR

CONTENTS

PART ONE THE PLANNING AND PREPARATION OF CORROSION TESTS INTRODUCTION 1

1. Metallurgical Factors, *H. S. Campbell* 5
2. Statistical Planning and Analysis, *F. H. Haynie* 31
3. Statistical Design of Experiments, *C. E. Makepeace* 59
4. Statistical Treatment of Nonnormally Distributed Stress-Corrosion Data, *J. H. Harshbarger, A. I. Kemppinen, and B. W. Strum* 87
5. Corrosion Data Reliability, *A. deS. Brasunas and C. B. Sonnino* 101

PART TWO LABORATORY CORROSION TESTING INTRODUCTION 113

6. General Tests and Principles, *D. H. Thompson* 115
7. Galvanic Corrosion Test Methods, *A. Gallaccio* 143
8. Electrochemical Methods, *S. W. Dean, Jr., W. D. France, Jr., and S. J. Ketcham* 171
9. Testing *in Vivo*, *V. J. Colangelo* 217
10. Stress-Corrosion Cracking, *H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper* 231
11. Testing at High Temperature, *L. R. Scharfstein and M. Henthorne* 291
12. Testing in Hot Brine Loops, *R. J. Hart* 367
13. Testing Nuclear Materials in Aqueous Environment, *W. E. Berry* 379
14. Liquid-Metal Test Procedures, *R. L. Klueh and J. H. DeVan* 405

15. Sensitized Coupons in Steam Acceptance Tests, *J. G. Goodwin, R. D. Gray, and L. F. Collins* 435
16. Evaluating Erosion (Cavitation) Damage, *J. Z. Lichtman, D. H. Kallas, and A. Rufolo* 453

PART THREE FIELD AND SERVICE TESTING
INTRODUCTION 473

17. Atmospheric Tests, *S. K. Coburn* 475
18. Seawater Tests, *K. G. Compton* 507
19. Testing in Hydrospace, *F. M. Reinhart* 531
20. Testing in Fresh Waters, *B. R. Pathak* 553
21. Tests in Soils, *W. P. Iverson* 575
22. Plant Corrosion Tests, *C. P. Dillon, A. S. Krisher, and H. Wissenberg* 599
23. Methods in Oil-Refining Industries, *A. S. Couper* 617
24. Testing Automotive Engine Coolants for Corrosion Inhibition, *L. C. Rowe* 625
25. Testing Corrosion Resistance of Coatings, *F. P. Helms* 647

PART FOUR EVALUATION OF CORROSION EFFECTS
INTRODUCTION 659

26. Potential-pH Diagrams and Metallic Corrosion, *M. Pourbaix* 661
27. Assessing Corrosion of Electroplated and Anodized Specimens, *V. E. Carter* 689
28. X-Ray Diffraction Methods for the Analysis of Corrosion Products, *R. S. Mapes and W. W. Berkey* 697
29. Evaluating Corrosion Inhibitors, *H. Kerst* 731
30. Radioactive Tracers for Inhibitor Evaluation, *A. Aladjem and J. Yakalom* 759
31. Use of the Electron Probe Microanalyzer, *F. E. Loftin* 769
32. Ellipsometry in Corrosion Testing, *J. Kruger and P. C. S. Hayfield* 783
33. The Single Crystal in Corrosion Testing, *H. Leidheiser* 833

Author Index 841

Subject Index 857

Part One

The Planning and Preparation of Corrosion Tests

Proper planning is essential for meaningful results in corrosion testing. Preliminary time and effort spent in consideration of metallurgical factors, test variations, statistical treatment, and reliability of results often are the most useful part of the test procedure.

Metallurgical differences in test metals must be clearly documented and understood. Chemical analyses for two test materials usually must be supplemented by a knowledge of the metallurgical history, including heat treatment, surface condition, aging, sample form and variations, metal shape or gauge, and variation within the given batch of material. A detailed and complete metal history is most useful in all testing.

If we can assume that we know enough about the test metal, we then can proceed to determine how many specimens are required for reliable testing. Although duplicate or triplicate samples should always be preferred to a single specimen, there are occasions when the variables concerned may require as many as 13 replicates. Since variations will always exist even between two presumably identical samples, statistical methods enable us to detect the significance of test results as distinct from the normal differences we must expect in any test.

The time to apply statistics is at the time tests are planned. Random sampling techniques and proper use of control replicates enable us to obtain reliable indications of the changes due to corrosion.

In any corrosion test, the selection of the most suitable test is essential. The method should involve the actual service environment where possible. Any attempt to use the so-called accelerated test to predict service performance is generally of doubtful value. Laboratory tests are useful for screening candidate materials, but these should always be considered to be preliminary in nature. Valid corrosion testing can be obtained only in the actual service environment and under actual service conditions.

Such factors as specimen size, metallurgical condition, replication, randomization, and reliability of test results are discussed in detail in Chapters 1 through 5.

As a starting point in corrosion testing, the engineer or scientist should familiarize himself with the accepted nomenclature in the field. The following definitions (from ASTM Method G 15-70) are listed as useful references.

Anode. The electrode of an electrolytic cell at which oxidation is the principal reaction. (Electrons flow away from the anode in the external circuit. It is usually the electrode where corrosion occurs and metal ions enter solution.)

Anion. A negatively charged ion.

Cathode. The electrode of an electrolytic cell at which reduction is the principal reaction. (Electrons flow toward the cathode in the external circuit.)

Cathodic corrosion. Corrosion of a metal when it is a cathode. It usually happens to amphoteric metals as a result of a rise in pH at the cathode or as a result of the formation of hydrides.

Cation. A positively charged ion.

Concentration cell. An electrolytic cell, the emf of which is caused by a difference in concentration of some component in the electrolyte. This difference leads to the formation of discrete cathode and anode regions.

Corrosion potential. The potential of a corroding surface in an electrolyte relative to a reference electrode measured under open-circuit conditions.

Electrolytic cleaning. A process of removing soil, scale, or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath.

Equilibrium (reversible) potential. The potential of an electrode in an electrolytic solution when the forward rate of a given reaction is exactly equal to the reverse rate. The equilibrium potential can only be defined with respect to a specific electrochemical reaction.

Galvanostatic. Pertaining to an experimental technique whereby an electrode is maintained at constant current in an electrolyte.

Inhibitor. A chemical substance or combination of substances which, when present in the proper concentration and forms in the environment, prevents or reduces corrosion.

Long-line current. Current which flows through the earth from an anodic to a cathodic area of a continuous metallic structure. Usually used only where the areas are separated by considerable distance and where the current results from concentration-cell action.

Metallizing. See Thermal spraying.

Open-circuit potential. The potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from it.

Overvoltage. The change in potential of an electrode from its equilibrium or steady state value when current is applied.

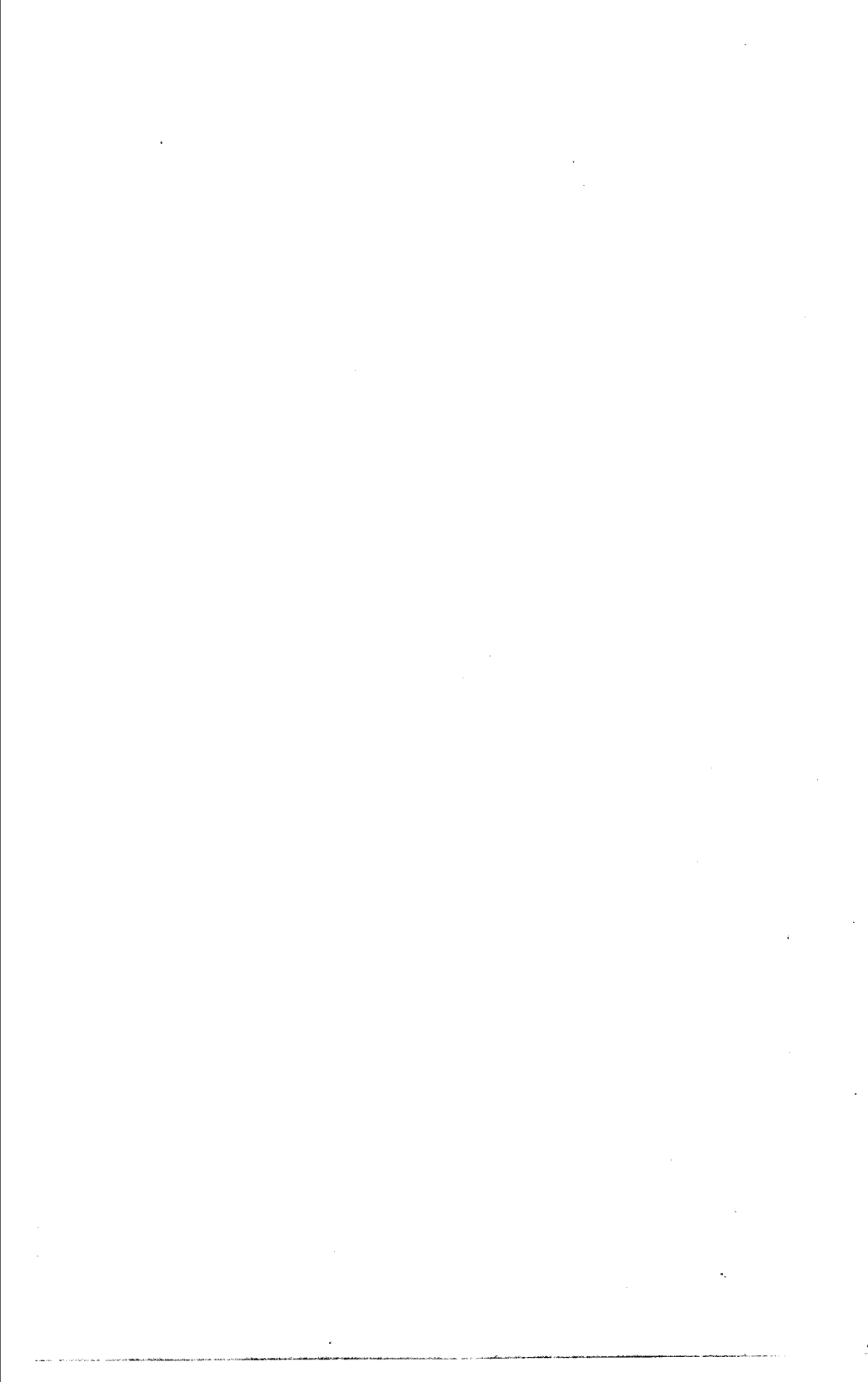
Passivator. A type of inhibitor which appreciably changes the potential of a metal to a more noble (positive) value.

Potentiostat. An instrument for automatically maintaining an electrode at a constant potential or controlled potentials with respect to a suitable reference electrode.

Redox potential. The potential of a reversible oxidation-reduction electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given electrolyte.

Stress-corrosion cracking. A cracking process requiring the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion which can disintegrate an alloy without either applied or residual stress.

Thermal spraying. A group of processes wherein finely divided metallic or nonmetallic materials are deposited in a molten or semimolten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire, or molten materials.



I

METALLURGICAL FACTORS

*Hector S. Campbell**

INTRODUCTION

Metallurgical differences among samples of the same alloy, arising from differences in their previous thermal and mechanical treatment or from fabrication processes such as welding, can have a great effect on overall corrosion resistance and on mode of corrosion. Metallurgical effects are usually intimately tied up with compositional factors, especially with the minor alloying elements or major impurities present. Compositional factors often control the effects of mechanical and thermal treatment on the nature and distribution of minor phases present in the alloy and on grain size and grain shape after working. It is therefore essential that reports of results of corrosion tests, or of the service behavior of alloys under corrosive conditions, should include the fullest possible details on the composition and metallurgical condition of the material concerned. Metallurgical effects are usually recognized and taken into consideration in stress corrosion or corrosion fatigue tests—if only because of their influence on the mechanical properties of the material. These effects are too often ignored and essential data consequently not recorded in corrosion tests that do not involve stressing.

The most important of the metallurgical factors that may need to be considered and recorded are discussed below in general terms. Those factors particularly important in different alloy systems and in weldments are then considered in greater detail.

* Metals Users' Consultancy Service, The British Non-Ferrous Metals Research Association, London.

FACTORS TO BE CONSIDERED

The possibility that metallurgical differences may affect corrosion behavior increases as we move from homogeneous single-phase alloys to duplex or multiphase alloys. This possibility is probably greatest in the heat-affected zones of multiphase, precipitation-hardened alloys that have been welded.

In homogeneous single-phase alloys the extents of cold work, grain size, and grain shape are the only metallurgical factors to be considered. Cold work can be important in situations where stress corrosion is possible, because it introduces residual stresses which may be sufficient to cause stress-corrosion cracking in the absence of any applied or working stresses. Theoretically the disordered structure produced by cold working should be more readily attacked and consequently anodic to areas on the metal surface that have not been worked. This effect is very rarely significant in practice, and comparison of the solution potentials of annealed and heavily worked samples of the same alloy shows the differences to be not more than 1 or 2 mV. Grain size and grain shape are also of little significance in the corrosion of this type of alloy except when the conditions favor intergranular corrosion or stress corrosion following an intergranular path. Under these conditions the greatest penetration will occur in specimens with a large equiaxial grain structure.

In duplex or multiphase alloys the amount and distribution of the most anodic phase will often determine corrosion behavior. The most undesirable condition is the presence of the anodic phase in the least amount that still permits it to form a continuous network. Corrosion tests on alloys in this condition will give low weight-losses, but metallurgical examination or measurement of the change in mechanical properties reveals the true extent of the corrosion damage. If the alloy contained about 50% of the anodic phase, the weight loss under the same test conditions might well be greater but the real damage comparatively slight. It is clear therefore that the metallurgical condition of a corrosion test specimen, and the consequent character of the attack on it, must be taken into account when deciding the most appropriate method of assessing the test results.

Obviously, the proportions of major alloying elements present play a primary role in determining the amount of the anodic phase that can be formed. The anodic phase present will depend also on the thermal history of the sample and sometimes on the minor alloying elements. These two factors will also affect the distribution of the anodic phase. Apart from these effects, the distribution of phases in a cast sample will be different from that in an extruded sample or in a rolled sample of the same alloy. The corrosion behavior of the material in the three forms is therefore also

likely to differ. It is important also to remember that in long-term tests or tests at elevated temperatures the amount and character of the phases present may change during the test. Control specimens must therefore be stored for the duration of the test under similar thermal conditions but outside the corrosive environment if the effects of corrosion are to be distinguished from those of time and temperature. All these factors are discussed in greater detail under the alloy systems for which they are of particular importance.

In multiphase heat-treatable alloys, variations in the nature and distribution of the hardening precipitate and of the solute-depleted zones introduce further possibilities for the metallurgical condition to affect corrosion behavior. These effects can arise from variations in the solution treatments or aging treatments. They are particularly important in aluminum alloys of the Al-Cu system (series 2000 alloys) and the high- and medium-strength Al-Zn-Mg alloys of the 7000 series. In these alloys such factors have been studied particularly with reference to stress-corrosion cracking and exfoliation corrosion. It is not usually possible to define the metallurgical condition of these alloys in terms of their microstructure—some of the more significant features being observable only by electron microscopy and still the subject of controversy. It is therefore necessary to quote the composition and history of the material as fully as possible if corrosion and stress-corrosion results are to be of maximum value to other workers. Not only the times and temperatures of solution and precipitation treatments but the quench rate, extent of any stretching after solution treatment, and even the rate of heating up to aging temperature are important. Grain size, the extent of recrystallization, and the relationship of the corrosion test specimen to the direction of working are factors that should be recorded in any tests on these alloys, especially in stress-corrosion tests. A material may appear immune to stress corrosion if tested in the longitudinal direction (i.e., parallel to the direction of rolling or extrusion) yet show high susceptibility if tested in the short transverse direction. These points are all discussed in greater detail in the section on aluminum alloys in this chapter.

Welding introduces further complications by changing the metallurgical condition of the parent metal in the heat-affected zone as well as by changing the composition of the metal in the fusion zone. The effects in the heat-affected zone vary from local overaging a short distance from the weld bead to the production of microscopic cracks in the region immediately adjoining the fusion zone where partial melting of the parent metal takes place. These and other features of welds in relation to corrosion and stress-corrosion performance are discussed in the section on welding and brazing.