Forms of Corrosion
RECOGNITION AND PREVENTION

C.P. Dillon, Editor

Volume 7

Contents

Preface

Forms of Corrosion—Recognition and Prevention, NACE Handbook Number One, was commissioned by the NACE Publications Committee as the first of a series of handbooks for the corrosion engineer. The committee gratefully acknowledges the work of the editor and chapter authors which made this handbook possible.

The Publications Committee believes the usefulness of this handbook can be greatly enhanced by the addition of more case histories. Their intention is to issue a revised edition as quickly as a substantial number of additional case histories are obtained. To this end, the Committee will pay $10.00 for each case history submitted that is selected to be included in the next edition.

To be considered, a case history must include all the information needed to satisfy the format used in this book, i.e., Phenomenon, Group/Type, Equipment, Conditions, Time to Failure, Illustrations, Comments, and Remedy. Illustrations submitted must be glossy black and white prints.

Submit your case histories to the NACE Publications Committee, P. O. Box 218340, Houston, Texas 77218.

Introduction

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THE PURPOSE of this manual is to introduce the reader to the eight forms of corrosion and to illustrate their macro-and micro-appearance as they occur in conventional engineering metals and alloys. Diagrams are occasionally employed to illustrate mechanisms, but photographs and photomicrographs are employed wherever possible, together with Case Histories in sufficient detail to enable understanding of the particular problems and the means taken to ameliorate the situations.

The editor and authors have elected to follow the classifications of corrosion popularized by Dr. Mars G. Fontana,[1] except that crevice corrosion and pitting are considered in one category (i.e., Localized Corrosion), permitting the use of the eighth grouping to embrace certain high temperature phenomena.

The eight forms of corrosion overlap to some extent. For example, De-Alloying (sometimes called Parting Corrosion in older texts) may follow a uniform mode (e.g., "layer-type dezincification") or may be highly localized (e.g., "plug-type dezincification"). Galvanic or "Two-Metal" corrosion may manifest itself either as general or uniform corrosion or as localized attack, depending upon geometry and conductivity in a specific situation. One type of corrosion may mitigate another, as when erosion-corrosion of heat exchanger tubes at the inlet end is diminished by the galvanic influence of the water-box.

In the following chapters, phenomena which are not clearly identified as belonging to one of the eight categories have been assigned to a particular chapter by mutual agreement between the editor and authors.

Forms of Corrosion

The eight forms of corrosion (Figure 0.1) may be divided into three categories:

Group I — Those readily identifiable by visual examination.

Group II — Those which may require supplementary means of examination.

Group III — Those which usually should be verified by microscopy of one kind or another (optical, scanning electron, etc.). These are sometimes apparent to the naked eye.

Group I

1. Uniform Corrosion. This type of general corrosion is characterized by an even, regular loss of metal from the corroding surface. All metals are subject to this type of attack under some conditions. It is the most desirable form of corrosion insofar as it lends itself most easily to predicting the life of equipment.

2. Localized Corrosion. In localized attack, all or most of the metal loss occurs at discrete areas. Pitting may occur on a freely exposed surface of a metal or alloy where the surface is non-homogeneous [has local cells set up by metallurgical differences (composition and structure of the metal)] under deposits of foreign matter or at imperfections in a film or coating.

Crevice corrosion is a particular form of pitting, usually induced between faying surfaces (e.g., nuts and bolts, riveted joints, threaded connections, flange surfaces, etc.), usually due to localized differences in the environment, for example, oxygen concentration cells or metal ion cells.

3. Galvanic Corrosion. This type of attack is occasioned by electrical contact between dissimilar

conductors in an electrolyte (e.g., copper and steel in water). The intensity of corrosion depends primarily on the difference in solution potential between the materials — the further apart in the Galvanic Series, the greater the possible corrosion of the anodic member of the galvanic couple — and secondarily on the effects of relative area and geometry. Conductive films may also cause a galvanic effect on metals (e.g., Fe304, "magnetite" or "mill-scale" on steel; lead sulfate films on lead in sulfuric acid), and conductive nonmetals like carbon can function as cathodes to metallic anodes.

Group II

1. Velocity Effects. Erosion-corrosion is attack accelerated by high velocity flow, either washing away otherwise protective films or mechanically disturbing the metal itself. The true nature of the attack, especially the differentiation of the effects of particulate matter in the stream, may require supplementary microscopy, despite the characteristic flow patterns visible to the naked eye.

Cavitation is a special form of attack, damage caused by the collapse of bubbles formed at areas of low pressure in a flowing stream.

Fretting is caused by vibratory relative motion of two surfaces in close contact under load. The nature of the wear and determination of the presence of minute oxidation products may require microscopic examination.

2. Intergranular Corrosion. Preferential attack of small areas at the grain boundaries in the metal structure may permit physical removal of whole grains ("sugaring"), although only a small amount of metal is actually dissolved. This may be apparent to the naked eye, but more often optical microscopy at least is required to confirm the mode of attack.

3. De-Alloying Corrosion. This type of corrosion is the selective dissolution of one component of an alloy, for example, zinc from yellow brass, leaving a pseudomorph of the original artifact. Because the dimensions are substantially unchanged, mechanical probing or microscopy is usually required as a supplement to the visual inspection.

Group III

1. Cracking Phenomena. These include both corrosion fatigue, a mechanical phenomenon enhanced by nonspecific corrosive environments, and environmental cracking, in which a brittle failure is induced in an otherwise ductile material under tensile stress in an environment specific for the alloy system. Environmental cracking is a broad category, which the editor and authors have decided should embrace true stress corrosion cracking, hydrogen induced cracking of various kinds, and liquid metal cracking.[1] Any cracking type failure should be diagnosed using at least optical microscopy. A scanning electron microscope is a valuable tool for differentiating the more obscure forms of attack, such as intergranular stress corrosion cracking from hot-short cracking, and transgranular SCC from corrosion fatigue.

[1]Ductility of a material is decreased by contact with a liquid metal.

2. High Temperature Corrosion. Although this can sometimes be identified by simple visual observation, more often a microscopic examination is required. This is due to subsurface phenomena within the matrix of the alloy, as well as obscured relations at the interface of the alloy with the surface films formed in many high temperature exposures.

3. Microbial Effects. Certain types of bacteria or microbes can influence corrosion when their metabolism produces corrosive species in an otherwise innocuous environment, or when they

produce deposits which can lead to electrochemical attack. Most often, the ultimate effect is some form of localized corrosion, but a biochemical analysis is required (rather than simple microscopy) to identify the offending organism.

Corrosion Prevention Techniques

There are basically five forms of corrosion control. Total prevention is rarely achieved, although it can be in specific instances, and the concept of corrosion control includes a broad spectrum of techniques ranging from acceptance of a finite life (in the case of optimum materials in a selected process) to some quantitative diminution of the rate of attack, for example, in inhibited cooling water systems.

1. Change of Materials. Besides the obvious total change of materials of construction, we include here partial changes like safe-ending of condenser tubes or installation of impingement plates, as well as massive surface changes such as lining, cladding, weld overlay and heavy duty organic or inorganic layers.

2. Change of Environment. One may change the total environment, as in from water-cooled to air-cooled heat exchangers, or alter or modify its nature by pH control, deaeration, use of chemical additives, or inhibitors.

3. Barrier Films. The application of a thin, corrosion resistant film between the metal and its environment (examples are hot-dipped or electroplated metal coatings, organic coatings, paints, etc.).

4. Electrochemical Techniques. These inclue the use of sacrificial coatings as well as cathodic or anodic protection by induced potentials in certain applications.

5. Design. In addition to the use of corrosion allowances for anticipated general or uniform attack, these techniques include physical layout (proper placing of nozzles or other vessel internals) and control of such influencing factors as velocity, temperature, vibration, heat flux, residual stress, etc.

Alloy Groupings

For ease of reference and to simplify discussion, the editor and authors have divided the common metals and alloys into ten groupings which more or less separate them by their corrosion characteristics.

The groups are numbered and identified as follows (Note: the group identification number is used also as the second number in the Case Histories in each Chapter):

1. **Light Metals**. Magnesium, Aluminum.
2. **Ferrous Metals**. Cast irons and alloy cast irons, Carbon steel, Low alloy steels, Alloy steels.
3. **Stainless Steels**. Martensitic, Ferritic, Superferritic, Austenitic, Precipitation-Hardening, Special grades.
4. **Lead, Tin and Zinc**.
5. **Copper, Brass and Bronzes**.
6. **Nickel and Its Alloys**.
7. **Chromium-Bearing Nickel Alloys**. N06600 (Alloy 600), N06625 (Alloy 625), N06007 (Alloy G), N10276 (Alloy C276).
8. **Cobalt-Based Alloys**.
9. **Reactive Metals**. Titanium, Zirconium, Tantalum.
10. **Precious Metals**. Silver, Platinum, Gold.

Environments

For purposes of discussion, the environments of concern are broken down into four categories, as follows:

1. Atmospheric Exposure. Incudes not only natural environments (traditionally considered to be rural, marine or industrial; or some combination of these), but also specifically contaminated atmospheres such as those containing hydrogen sulfide, ammonia, sulfur dioxide, etc.

2. Aqueous Environments. Includes natural or industrial waters, as well as extremely dilute solutions of inorganic or organic chemicals.

3. Soil. Includes underground installations of piping or vessels and the soil-side of structures such as tank bottoms.

4. Process. Includes organic or inorganic syntheses and other processing environments that affect materials.

Unless an author has chosen to discuss one or more of these in his introduction for purposes of illustration, environmental effects are confined to the Case Histories in which they are identified by the third digit. For example, Case History No. 1.3.4.1 refers to general corrosion (13.4.1) of stainless steel (1.3.4.1) in a process stream (1.3.4.1). The last digit is the numerical sequence number, i.e. this is the first Case History in this category (1.3.4.1).

It is the purpose of this manual to aid the reader in the recognition of phenomena, the susceptibility of the different groups of metals and alloys to certain types of corrosion, and the applicability of the several types of corrosion control in specific problems. It must be emphasized, however, that the ultimate solution of a corrosion problem requires professional counsel and a suitably sophisticated economic appraisal of the several possible alternatives.

Reference

1.Fontana, M.G., "The Eight Forms of Corrosion," *Process Industries Corrosion*, pp. 1-39, NACE (1975).

GROUP I

General Attack

original surface

Localized Attack

Localized Corrosion

Pitting

Crevice Corrosion

Galvanic Attack

base metal   noble metal

GROUP II

Velocity Phenomena

Erosion

flow

Cavitation

bubbles

Fretting

load

vibr.

Intergranular Attack

Weld Decay

HAZ   weld

FIGURE 0.1 — Eight Forms of Corrosion (Mechanics of Attack)

Group II (continued)

Exfoliation

De-Alloying Attack

layer   plug

GROUP III

Cracking Phenomena

Stress Corrosion Cracking

static
stress

Corrosion Fatigue

dynamic
stress

High Temperature Attack

Scaling

scale
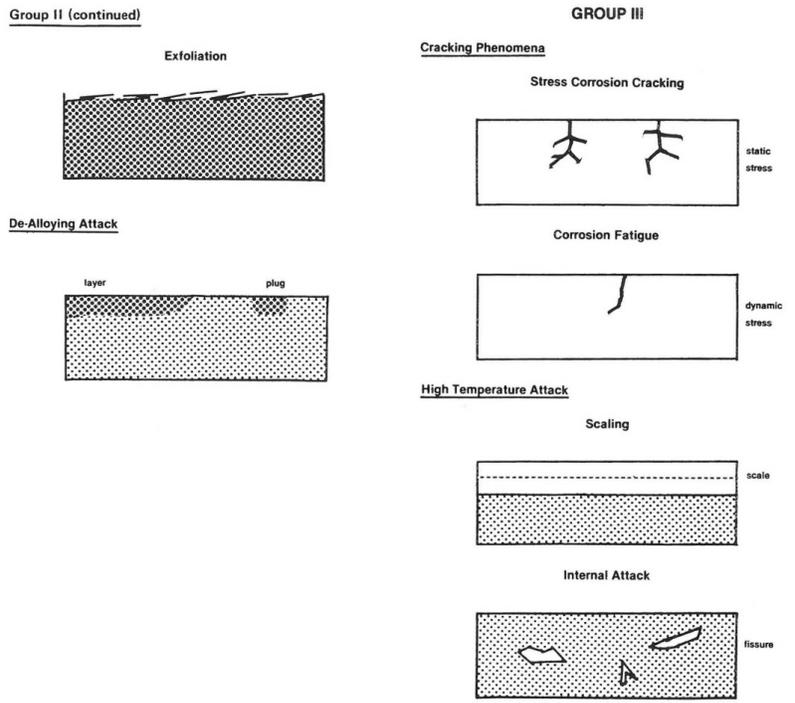
Internal Attack

fissure

FIGURE 0.1 — Eight Forms of Corrosion (Mechanics of Attack) Continued

Chapter 1
General Corrosion of Metals

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Definition and Description

GENERAL corrosion is corrosion that proceeds without appreciable localization of attack. For sheet or plate materials, this leads to relatively uniform thinning. For round bar or wires, corrosion proceeds radially inward at essentially a uniform rate around the entire circumference. The result is the production of a bar or wire of progressively smaller diameter. Pipe and tubing which suffer general corrosion are thinned from one side or the other (or both), depending upon the nature of exposure to the corrosive environment. Misapplication of materials in corrosive environments often results in severe general corrosion.

Categories of General Corrosion

Category I

General corrosion proceeds due to the solubility of corrosion products, at a rate determined by the electrode potential of the metal in the particular environment and the kinetics of the situation (e.g., steel in air-saturated water, lead in acetic acid, copper in soft waters containing aggressive carbon dioxide).

Category II

A passivating barrier coating is formed which stifles further attack. Referring to the Pourbaix Diagram[1] for iron (Figure 1.1) in regions of electrode potential and pH in which a solid reaction product is thermodynamically stable, there is the possibility that it will also be protective. (Note: It must be emphasized that protectiveness must be demonstrated; it cannot safely be assumed.) If the reaction product film is protective, the reaction rate will slow down rather quickly, and further corrosion will be stifled. Thus, a passive material can corrode thermodynamically, but doesn't continue to do so in practice. The material is not inert, but corrodes at a low rate to continually repair the passive film.

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[1]A Pourbaix diagram relates thermodynamics to corrosion phenomena by means of pH-potentiai plots. They are constructed from calculations based on the Nernst equation and solubility data for various metal compounds.

Typical or passive behavior is the performance of stainless steels, aluminum and titanium, which rely on a practically invisible surface film of metallic oxides for their everyday corrosion resistance.

Examples of this phenomenon also include the tarnishing of silver, the formation of a protective films on magnesium in hydrofluoric acid, and the formation of insoluble sulfate films on steel and lead in cold concentrated sulfuric acid. It should be noted that such films may be readily disturbed under flow conditions, leading to erosion-corrosion, as discussed in Chapter 5.

Category III

The metal or alloy is "immune" to attack in the environment of choice. Stated another way, the thermodynamic activity of the metal ion species at equilibrium is negligibly small.

On the Pourbaix Diabram (Figure 1.1), the "immune" region is bounded on the "active" side by a metal/metal ion coexistence line, which is calculated by selecting a permissible ionic activity for the

ion which represents "no corrosion for all practical purposes." Often, this ionic activity is selected as 10^{-6}. However, in practice, any permissible activity may be chosen which suits the application.

Examples of immune behavior include gold exposed to the atmosphere, low carbon steel in completely deaerated water, and, in some cases, tin in sealed food containers. The electrode potential of each of these materials is in the immune region of the appropriate Pourbaix Diagram.

Category IV

This comprises the special case of artificially controlled uniform dissolution processes. Referring again to Figure 1.1, in regions of electrode potential and pH in which an ionic species is the only stable species, uniform chemical dissolution is thermodynamically favored. Advantage may be taken of this in the design of commercial processes such as chemical machining or electropolishing, in such cases, care must be taken with alloys (as opposed to pure metals) to avoid dealloying phenomena (i.e., selective loss of certain alloying constituents; cf. Chapter 7).

Considerable commercial use is made of chemical machining in fabrication of aluminum alloy airframe parts, and for the shaping of coiumbium Cb752. Another example
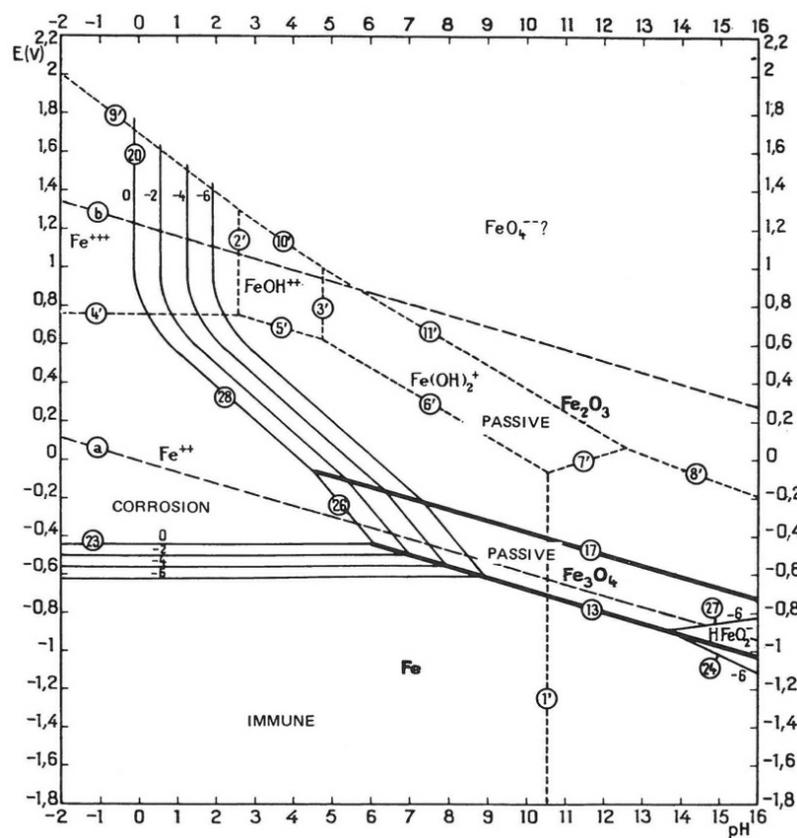

FIGURE 1.1. — Potential pH equilibrium diagram for the system iron-water, at 25 C (considering as solid substances only Fe, Fe30, and Fe203).

is the electropolishing of austenitic stainless steel chemical equipment to improve either corrosion resistance or anti-stick properties.

Methods of Corrosion Control

Of the many forms of corrosion, general attack is the least insidious, since the life of a part subject only to truly uniform attack should be readily predictable.

The progress of metal wasteage is linear with time, and the rate of penetration (or of thinning to the point where operating pressure can still be reliably contained) can be calculated either by equipment measurement (for example, wall thickness at specific intervals) or from corrosion data. For example,

a corrosion rate of .13 mm/y (5 mpy) would result in a metal loss of 1.52 mm (.060") in a twelve-year period. A corrosion allowance of 1.59 mm (1/16 of an inch) is often adequate to provide twelve years service in process exposures, perhaps 25 years in storage tanks. On the other hand, a 14 BWG heat exchanger tube of 2.11 mm (.083") wall can probably tolerate no more than a 50% loss of thickness (e.g., 1.02 mm or 40 mils in eight years at a rate of .13 mm/y or 5 mpy).

All of the corrosion control measures discussed in the Introduction are applicable.

If the rate of attack is unacceptable — when it cannot reasonably be handled by a corrosion allowance, or where metal contamination cannot be tolerated — a total change in materials, or a massive surface change, such as lining, cladding or weld overlay is indicated. Partial changes are not generally applicable, being used more often for more localized forms of attack.

Changes of environment are often employed, especially in the use of inhibitors, pH control, deaeration, etc.

Barrier films are employed in metallic form and, more often, as paints or coatings designed to protect ferrous metals particularly against atmospheric or aqueous corrosion.

In the electrochemical realm, if the metal must remain essentially film-free (i.e., Category III), the electrode potential must be maintained in the immune region of the Pour-baix Diagram (for pure metals). One way to accomplish this is by application of cathodic protection. However, materials subject to hydrogen embrittlement or hydrogen induced cracking (hardened alloy steels or martensitic stainless steels) should not be polarized below the potential of the equilibrium hydrogen electrode. Inhibitors such as filming amines may be useful.

With proper combinations of metals and environments, anodic protection to move the electrode potential into a "passive" region on the Pourbaix Diagram will provide the conditions necessary for Category II, that is, a protective film of corrosion products. An example of this is the protection of steel tanks and of S31600 (AISI 316) coolers in sulfuric acid service. (Note: Addition of strong oxidants or alternations of pH can induce the same electrochemical shift under certain conditions.)

Design against uniform corrosion is usually a consideration only in the sense of providing a suitable corrosion allowance, or a suitable corrosion resistant material in the first place. Accelerated uniform corrosion may occur due to contamination or from recycling a process stream, for example, the "activation" of S31683 (AISI 316L) in acetic acid service by chloride ion contamination. Accelerated attack may also occur due to "hot-wall" effects, wherein a metal surface transferring heat corrodes at a markedly higher rate than the same material under simple immersion conditions in the same environment. Under such circumstances, the only improved design (short of a change in tube material) is a larger exchanger designed to minimize the heat-flux across the tubes.

Performance of Alloy Groupings

Table 1.1 lists some examples of uniform corrosion. In addition, certain generalized remarks are offered below regarding the particular alloy groupings.

Table 1.1 — Examples of Uniform Corrosion in Metal Systems

Spontaneous

Tarnish of silver flatware.

Tarnish of electrical contacts.

Architectural examples:
   Patina on copper.
   Weathering steels.
   Special treatments: lemon oil on statuary bronze, anodizing
       to get "built-in color", i.e., grey for Al-Si alloys and gold
       for Cr in Al alloys.

Etching treatments:
   Metal cleaning (surface renewing types).
   "Bright Etches" for reflective surfaces.
   Surface preparation for painting: wash coat primers and
       chemical conversion coatings.
   Chemical machining.

Applied

Electrochemical processes:
   Anodizing of Al, Ti, Stainless steels, Mg, etc.
   Electropolishing.

Surface altering processes which can cause corrosion to be
uniform:
   Ion implantation.
   Vapor deposition.
   Calorizing.
   Chromizing.
   Electro-plating.

Pseudo-Uniform Corrosion

Alclad products.

Galvanized steel.

Aluminized steel.

Light Metals

Magnesium alloys are subject to attack in acid and neutral solutions, and show passive behavior in alkaline solutions due to the formation of magnesium hydroxide ($Mg(OH)_2$). One notable exception to acid attack is the resistance in hydrofluoric acid, which forms a protective film of insoluble magnesium fluoride, stifling further attack.

Aluminum alloys owe their corrosion resistance to the presence of a naturally formed oxide film. Consequently, under conditions in which the passivating film is thermodynamically stable, corrosion tends to be localized at sites of damage or breakdown of the film. Because of the amphoteric nature of aluminum, general attack occurs in strongly acid or strongly alkaline environments. In such environments, attack occurs at sufficiently high rates that only short term exposures are permissible,