

Corrosion

in the

Petrochemical

Industry

Second Edition

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Corrosion in the Petrochemical Industry

Second Edition

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

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Preface to the Second Edition

According to NACE International, the total annual cost of corrosion in the oil and gas production industry is estimated to be \$1.372 billion. This breaks down into \$589 million in surface pipeline and facility costs, \$463 million annually in downhole tubing expenses, and another \$320 million in capital expenditures related to corrosion.

Because corrosion is such a significant issue, ASM International has devoted three *ASM Handbook* volumes to studying its causes, behavior, and prevention. *ASM Handbook*, Volume 13A, *Corrosion: Fundamentals, Testing, and Protection* (2003) helps readers understand corrosion, and Volume 13B, *Corrosion: Materials* (2005) dives into the corrosion

performance of materials and the selection and application of materials for corrosion resistance. Volume 13C, *Corrosion: Environments and Industries* (2006) looks at how corrosion affects specific segments of the world economy.

Originally published from several sources in 1994, this second edition of *Corrosion in the Petrochemical Industry* collects articles from Volumes 13A and 13C. These peer-reviewed articles were written by experts in the field of corrosion and were specifically chosen for this book because of their relevance to the petrochemical industry. ASM is grateful to the many volunteers who contributed to this effort.

Preface to the First Edition

Corrosion in the Petrochemical Industry collects together authoritative, peer-reviewed data and information on corrosion in the petroleum, petrochemical, and chemical processing industries from a number of ASM International publications. The principal sources are *Corrosion*, Volume 13, and *Failure Analysis and Prevention*, Volume 11, of the *ASM Handbook*. Other sources include the *Handbook of Corrosion Data*; *Handbook of Case Histories in Failure Analysis*, Volumes 1 and 2; and Metadex, the Materials Information database of materials abstracts. This information has been carefully selected and edited into one cohesive, comprehensive volume on corrosion phenomena in these industries.

This project was initiated because survey results and other input from ASM members and book buyers indicated a strong interest in collections of ASM data and information repackaged into logical, convenient new configurations. Based on this interest, a team of ASM staff members was assembled to gather additional input and then use it to craft a publication that is highly responsive to the demands of its intended audience. This team effort was led by Grace Davidson, with team members Steve Chang, Karen Germany, Scott Henry, Rich Majoros, Robert Pavlik, Dawn Summerlin, and Reva Zaretsky; Robert Uhl, Director of ASM's Education Department, sponsored the project.

The team chose the subject of corrosion because of the great amount of high-quality ASM published information available on this subject. The team conducted over 100 in-depth phone interviews with ASM book buyers who work or have an interest in the area of corrosion. The results of these phone interviews were then used as input for detailed quality function deployment matrices. (Quality function deployment is a systematic method for organizing and analyzing customer demands in order to develop products that are responsive to those demands.) Out of the quality function deployment process, the team developed three potential outlines, each with a separate area of focus in the field of corrosion. The team then went back to a small group of respondents to the original survey and asked them to review and comment on the outlines, and to rate them according to their apparent usefulness to a clearly defined audience.

The outline selected by this group was the one used to develop this volume. The outline and survey data were turned over to Linda Garverick, who has done a masterful job of compiling and editing the information to turn it into a cohesive, well-rounded publication. ASM International owes a debt of gratitude to the survey respondents who gave so generously of their time, opinions, and expertise to help develop this handbook. Of course, this book would not have been possible without the efforts of the dozens of experts who wrote and reviewed the information it contains.

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Introduction to Forms of Corrosion

WHILE CORROSION CAN TAKE MANY FORMS, it is most generally defined as a chemical or electrochemical reaction between a material and its environment that produces a deterioration (change) of the material and its properties. Organizing the forms of corrosion has the advantage that corrosion processes with similar mechanisms can be considered together. Categorization of the forms of corrosion has existed in various schemes for many years. A broad view would separate corrosion into two categories: corrosion that is not influenced by any other process and corrosion that is influenced by another process, such as the presence of stresses or erosion. A more focused view would categorize corrosion as uniform or localized, aqueous or gaseous, wet or dry, and so forth.

Uniform Corrosion

Uniform corrosion processes include many corrosion phenomena that are encountered in the practice of corrosion engineering and corrosion science. The majority of those phenomena deal with either aqueous or gaseous corrosion, although there are concerns about materials for use in molten salt and liquid metal environments. Gaseous corrosion is usually associated with high-temperature environments. Atmospheric corrosion is not considered a part of gaseous corrosion because the corrosion reaction occurs in a thin aqueous layer on the surface of the metal. Galvanic and stray current corrosion are not environment specific but rather can occur in any of the environments mentioned earlier.

Localized Corrosion

Localized corrosion is described as corrosion that occurs at discrete locations on a material. While this is true and accounts for the naming of this form of corrosion, it is also the localized state of the environment that causes the accelerated attack of materials. Thus the propagation of pits on passive metal surfaces, the aggressive attack where two metals overlap to form a crevice, and the distinctive filiform attack on metal surfaces coated with thin organic layers result from differences in the metallurgy of the alloy and because the localized chemistry of the environment is different from that of the bulk of the environment.

Mechanically Assisted Degradation

Mechanically assisted degradation involves processes where external interactions can influence the corrosion rate. Examples are fretting, cavitation, and impingement corrosion, and corrosion fatigue.

Environmentally Induced Cracking

Environmentally induced cracking is a form of corrosion in which the external influence on the corrosion process is stress. For stress-corrosion cracking, the stress is often externally applied. For hydrogen damage, liquid metal induced embrittlement, and solid metal induced embrittlement, the stress is induced by reactions with the environment.

In the time between the publication of the first edition of this book and this publication, considerable work has been done in the area of environmentally induced cracking. However, little gain has been made on the theory of the various cracking mechanisms, and certainly the same is true for progress in modeling or quantitative methods to predict cracking induced by the environment.

This section addresses the mechanisms of corrosion that produce cracking of metals and intermetallic compounds as a result of exposure to their environment. This cracking may take the form of relatively slow, stable crack extension with a predictable growth rate or, as is often the case, unpredictable catastrophic fracture.

Two types of cracking or embrittlement phenomena are discussed: stress-corrosion cracking (SCC) and hydrogen damage (frequently referred to as hydrogen embrittlement). In general, these different phenomena show many similarities, and it would at first seem appropriate to propose an all-encompassing mechanism to account for these behaviors. For example, both phenomena generally are dependent on yield strength and applied stress. As both of these factors increase, resistance to SCC, hydrogen damage, liquid-metal embrittlement, and solid metal induced embrittlement decreases. However, as presented in the discussion of each of these phenomena, many differences between the various forms of environmentally induced cracking are encountered, and in fact, substantial differences are observed for behavior of metals and alloys within a specific form of cracking.

At this time, the understanding of each of these mechanisms of cracking is largely

phenomenological. No satisfactory theory exists for any of these mechanisms that totally explains all behavior observed either under laboratory or field conditions. Although many theories that are specific to the behavior of certain alloy systems or environments exist, none is universal enough to explain, for example, the diverse behavior of hydrogen damage for systems that develop hydrides versus alloys of iron that do not form hydrides. There are many of these contradictory factors that impede the development of an all-encompassing theory.

Additionally, there has been a continuing controversy since the 1960s concerning the actual micromechanistic causes of SCC, which some investigators consider to be related to hydrogen damage and not strictly an active-path corrosion phenomenon. Although certain convincing data exist for a role of hydrogen in SCC of certain alloys, sufficient data are not available to generalize this concept.

Because satisfactory mechanistic models have not been developed for any of these forms of environmental cracking, the prediction of environmentally assisted cracking is essentially nonexistent. However, the need for prediction of these types of failures is most important, because observable and measurable corrosion usually does not occur before or during crack initiation or propagation. When corrosion does occur, it is highly localized such as pitting or crevice attack and may be difficult to detect.

Microbiologically Influenced Corrosion

The chapter, "Microbiologically Influenced Corrosion," discusses the interactions of the biofilms that form on virtually all structural metals and alloys immersed in aqueous environments. These interactions can lead to many of the forms of corrosion detailed previously but especially those associated with uniform and localized corrosion.

Metallurgically Influenced Corrosion

To understand *metallurgically influenced corrosion*, it is first important to understand what is meant by metallurgy. It has been described as "the art and science of procuring and adapting

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metals to satisfy human wants" (Ref 1). As such, it includes the recovery of metals from ores (extractive metallurgy), the formation of metals into various forms (mechanical metallurgy), and the understanding of the interaction of the chemical species, crystal orientations, and dislocations in metals and alloys (physical metallurgy). All of these processes can influence the composition, structure, stress level, and impurities in metals and alloys and, thus, their corrosion behavior. Another process, welding, is usually applied after metals are formed and shaped by metallurgical techniques. Welding produces localized changes in the composition, structure, stress level, and impurities in the joined metals and thus also can affect corrosion.

The fundamental understanding of electrochemical corrosion kinetics is based on the uniform dissolution of an unfilmed, pure, homogeneous metal that is equally exposed at all locations to a homogeneous environment. Corrosion engineers know that this description does not reflect reality in practical situations. In many engineering structures, dissimilar alloys are connected in a variety of ways, crevices often exist, and the environment is variable and dependent on local flow conditions. Furthermore, metals and alloys are typically covered with a surface layer. Their corrosion behavior is influenced by the surface layer and by a host of metallurgical factors. Even extremely pure single crystals have defects that can affect corrosion, but impurities and alloying elements, grain boundaries, second phases, and inclusions often have a dominant effect. Finally, welded structures almost always corrode first at the welds because of metallurgical heterogeneities that exist in and near welds. In general, the most susceptible site or defect on a metal surface will be the first to be attacked when it is exposed to a corrosive environment. Sometimes such attack simply results in innocuous removal of the susceptible material, leaving a surface with improved corrosion resistance. The most susceptible defects that lead to sustained attack will control the form of corrosion.

The corrosion resistance of stainless steels and nickel-based alloys varies markedly depending on the alloying elements and processing conditions. Under many conditions, stainless steels exhibit localized corrosion, which is greatly affected by the alloy composition and metallurgical factors. Pitting corrosion in stainless steels

often initiates at MnS inclusions owing to the reactivity of the sulfides and the effect of the S-containing dissolution products on the nearby passive film. The formation of carbides at grain boundaries can reduce corrosion resistance through the formation of susceptible Cr-depleted zones in the neighboring matrix. A continuous network of such Cr-depleted zones can render stainless steel sensitized, or extremely susceptible to sustained intergranular corrosion or stress corrosion cracking. Other phases, such as sigma and chi phases, can also be detrimental, especially in oxidizing environments. On the other hand, stainless steel does not always corrode by a localized form of attack. When a solutionized low-sulfur stainless steel is exposed to boiling nitric acid, the attack is not local in nature but rather is dominated by the orientation of the grains so that a stepped structure develops with the most susceptible orientations corroding faster.

The corrosion resistance of aluminum alloys is completely dominated by metallurgical factors. High-purity aluminum is rather resistant to corrosion in most neutral pH environments. The passive film is relatively insulating, protective, and noncatalytic. However, commercial aluminum alloys contain alloying elements, impurity elements, precipitated phases and intermetallic constituent particles. The precipitated phases and intermetallic particles can be anodic or cathodic relative to the matrix or can switch between the two with time as a result of selective dissolution. Anodic particles can be initiation sites for pitting corrosion, and cathodic particles can be active cathodes, supporting the cathodic reaction necessary for sustained attack. These phases can form at grain boundaries and result in a sensitized structure if the grain boundary precipitate or neighboring solute-depleted zone is susceptible to sustained attack. Wrought aluminum alloys often have an elongated grain structure, which can result in susceptibility to exfoliation corrosion or orientation-dependent stress corrosion cracking. Solid solution alloying of aluminum can alter the susceptibility to localized corrosion, either decreasing, as with copper alloying, or increasing the susceptibility as in the case of zinc alloying. Clearly, the metallurgical effects on the corrosion of aluminum alloys are varied and complex.

When an alloy composed of a solid solution of various elements corrodes, it is typical that

one or more elements dissolve preferentially, leaving other elements enriched on the surface. This dealloying process depends strongly on nonmetallurgical factors such as environment and potential. However, the dealloyed microstructure is vastly altered, often resulting in a reduction of strength and other properties.

Welded microstructures can be extremely complex and often change drastically over a very short distance. The fusion zone or weld metal is a dendritic structure that solidified from a molten state. Bordering the fusion zone are transition, unmixed and partially-melted zones, and the heat affected zone (HAZ). These zones can be reheated and altered by subsequent weld passes in multipass welding. For alloys with structures that depend strongly on thermal history, such as steels, the final microstructure can be extremely complex. Since welded structures are often quite susceptible to corrosion, over-alloyed filler metals are often used to enhance the weld corrosion resistance. For stainless steels with sufficiently high carbon content, sensitization in the HAZ is another major problem.

Corrosion is a reaction between a metal and its environment, and both are important in the process. The chapters presented here focus on the metal side of the corrosion reaction and describe a wide range of metallurgical factors that influence corrosion.

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Pitting Corrosion

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