Recognition and Analysis of Corrosion Failure Mechanisms

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ABSTRACT

Corrosion has a vast impact on the global and domestic economy, and currently incurs losses of nearly $300 billion annually to the U.S. economy alone. Because of the huge impact of corrosion, it is imperative to have a systematic approach to recognizing and mitigating corrosion problems as soon as possible after they become apparent. A proper failure analysis includes collection of pertinent background data and service history, followed by visual inspection, photographic documentation, material evaluation, data review and conclusion procurement. In analyzing corrosion failures, one must recognize the wide range of common corrosion mechanisms. The features of any corrosion failure give strong clues as to the most likely cause of the corrosion. This article details a proven approach to properly determining the root cause of a failure, and includes pictographic illustrations of the most common corrosion mechanisms, including general corrosion, pitting, galvanic corrosion, dealloying, crevice corrosion, microbiologically-influenced corrosion (MIC), corrosion fatigue, stress corrosion cracking (SCC), intergranular corrosion, fretting, erosion corrosion and hydrogen damage.

Keywords: Failure Analysis, Corrosion, Microscopy.

1. CORROSION AND THE U.S. ECONOMY

Recent economic studies have shown that the cost that corrosion incurs to the U.S. economy is in excess of $270 billion annually(1). This is equivalent to almost $1,000 for every man, woman and child in the country. This staggering liability is spread over a wide range of industries, including production, manufacturing, infrastructure, government, utilities and transportation. Things that make up this cost include replacement of equipment, loss of product, equipment maintenance and repair, excess capacity in the form of scheduled maintenance downtime, redundant equipment, corrosion control measures, technical support, design considerations, insurance premiums and extra equipment inventory, just to name a few(2). It is prudent to detect and mitigate corrosion problems as soon as possible in an effort to minimize fiscal damages. An effective way to do this involves using a proactive approach to attack a problem or potential problem as soon as it is detected, incorporating the use of modern analysis techniques, pertinent experience, engineering expertise and common sense. In this way, proper corrective actions can rapidly be put into place in order to prevent recurrence.

2. THE FAILURE ANALYSIS PROCESS

A logical and systematic approach is extremely important in determining the root cause of any failure, whether it is due to corrosion, fracture, wear, or any other mechanism. The use of such an approach will minimize the likelihood that important details and features will be overlooked during the course of the failure investigation, as such details may not be recoverable once the failed component has been dissected. Certain guidelines have been found useful for maximizing the chance of an accurate prognosis in a failure investigation.

Background Data Collection

The first logical step to any failure analysis is to gather as much background information as possible, as it relates to the failed component. Details such as part information and identification, including pertinent drawings and specifications, should be collected and kept on-hand for future reference. The known service history of the component is also important, and should include details about how the part was manufactured, as well as what stresses and service conditions the component experienced during its lifetime. In cases involving machines and equipment, details about the maintenance schedule and repair history should be recorded, along with any anomalous service events. Information about the frequency of the observed failure is also important, as it can provide clues as to whether the failure is due to production lot or unusual service conditions.

Initial Inspection and Scope Definition

With a good handle on the background information and component history, the initial inspection may be performed. This inspection should be done directly by the failure analyst in most instances; however, in cases involving large components or machinery, it may be more economical for it to be performed by reasonably experienced personnel who are familiar with the equipment. The initial inspection involves review of the failed component and adjacent components, including documentation of wear patterns, unusual surface damage, corrosion features, etc. Photographic documentation should also be conducted to clearly illustrate the nature of the problem and provide visual aides for the analyst to review and discuss. It is during this stage that the scope of the investigation is determined. The scope will be based upon parameters such as the available amount of time to complete the analysis, the number and condition of representative failed and non-failed components, and the available funds to complete the material evaluation.

Material Sampling and Shipment

Relatively small failed components can easily be shipped to a laboratory for in-depth analysis. Large components, however, will often need to be sectioned in order to facilitate shipping and handling. It is of great importance that the evidence not be damaged during the sectioning process, and that the failed areas be preserved in their original form as much as possible. In cases involving fractured components, careful sectioning practices should be employed to avoid damaging the fracture surface. It should be noted that some fractures could potentially be corrosion related; because of this, the use of cutting fluids and coolants should be minimized, as they will contaminate the corrosion deposits. If cooling is necessary to avoid altering the part microstructure, clean water should be used in lieu of cutting fluids. The size of the sample should also be considered, and adequate material should be removed as to allow for mechanical testing, as it may be appropriate. It is also prudent at this stage to photograph the failed component prior to and after the sectioning process, in order to clearly illustrate where the failed component was situated while it was in service. Once the samples have been extracted, they should be identified and placed into protective packaging materials prior to being sent to the laboratory.

Visual Inspection

Once the failed component has reached the laboratory, the analyst can proceed with the detailed visual inspection process. During this stage, careful observations are made as to the condition of the component and the appearance of the damage which apparently led to or contributed to the failure. Localized surface damage outside of the failed areas should also be characterized, as it may be suggestive of misalignment or anomalous service conditions. Low and high magnification photographic documentation should also be conducted at this stage to illustrate the morphology and color details. In cases where laboratory cleaning is necessary, the failed areas should be documented before and after cleaning, as the cleaning process can obscure the original color of any corrosion deposits. The component should also be photographed prior to and following any dismantling or sectioning. In cases involving corrosion where adequate amounts of corrosion products are present, such products should be physically sampled, either by light scraping, or by the use of acetate replicas. Care should be taken to preserve the original form of the corrosion deposits as much as possible, as they sometimes exhibit microscopic features that can give clues as to how they were formed. Whatever sampling method is used, it is imperative that the corrosion products not be contaminated.

Chemical Analysis

In most investigations, it is prudent to analyze the base material of the failed component for elemental makeup. Several different techniques are available for this process, and the appropriate technique depends on the material grade and component form. For relatively large, solid metal samples, techniques such as glow discharge spectroscopy (GDS) and optical emission spectroscopy (OES) have been established as accurate and reasonably inexpensive methods for chemical analysis. For smaller components, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) can be used. This analysis technique involves acid dissolution of clean machining chips or drillings from the metallic component, followed by analysis of the resulting solution. When completely nondestructive analysis is desired, approximate chemical compositions can be obtained using portable x-ray fluorescence (XRF), which involves the use of a hand-held analyzer. This technique is commonly used for positive material identification (PMI), but has limitations in accuracy and capability to analyze certain elements. Semi-quantitative elemental characterization of corrosion deposits can be performed in conjunction with scanning electron microscopy (SEM) using energy dispersive x-ray spectroscopy (EDS) or wavelength dispersive x-ray spectroscopy (WDS), where the emitted x-rays from the electron beam give information as to the approximate elemental composition of the target material. X-ray diffraction (XRD) can be used to identify compounds in corrosion deposits by analyzing crystal plane spacing. In studies involving organic substances, characterization can be performed using Fourier transform infrared spectroscopy (FTIR), in which the material is bombarded with light in the infrared (IR) spectrum, and the reflectance or absorbance pattern can be used to identify the nature of the material. Additional characterization using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) is sometimes necessary to more clearly identify the material. The former technique, TGA, gives a measure of the weight loss profile as a function of temperature, and this can be used to quantify the various components of the material. In the latter technique, DSC, the sample is slowly heated, and the temperature and heat flow associated with material transitions are measured. This provides quantitative and qualitative information about physical and chemical changes involving endothermic or exothermic processes, as well as changes in heat capacity.

Mechanical Testing

It is often incisive to measure the mechanical properties of a failed component, particularly in instances where fracture or wear are involved. Relatively common test methods are used to determine the durability of a material under a variety of stress and temperature conditions. Hardness can be used to provide an estimate of the ambient temperature ultimate tensile strength in most instances, although tensile testing can be performed at a variety of temperatures in order to directly measure the tensile strength, yield strength and ductility under a low strain rate. Conversely, impact testing can be conducted at a specified temperature or series of temperatures in order to characterize the fracture toughness at a very high strain rate. If the part is too small to allow for tensile or standard hardness testing, it can be prepared in a metallographic mount and subjected to microhardness testing, which can also be used to approximate the ultimate tensile strength. In cases involving formed parts, the formability of the raw material can be characterized using Olsen Cup testing, and the strain hardening exponent (n-value) and plastic strain ratio (r-value) of the material can also be measured using specialized tensile testing techniques.

Scanning Electron Microscopy

High magnification characterization of the component surface is conducted using a scanning electron microscope (SEM). This instrument allows for positive determination of the fracture mode in cases involving fractures, and also facilitates detailed characterization of corrosion features that cannot be discerned under light microscopy. This microscope enables the analyst to view the sample at magnifications of up to 5,000X in most circumstances. Under good instrumental conditions and in the absence of residual vibration, magnifications of 20,000X can reasonably be reached while maintaining high quality imaging; however, these magnifications are seldom needed for adequate characterization of the fracture or corrosion features. Some SEM's are equipped with an EDS or WDS feature, which enables elemental characterization of inclusions and corrosion deposits. This is useful for determining possible causes of the corrosion, as well as identifying the most likely corrosion mechanisms.

Cross Section Examination

A wide range of information can be obtained from evaluating a failed component in cross section. In cases involving fractures, cross section examination is commonly conducted at the fracture origin, in order to identify any material anomalies that may have served as crack initiation sites. In corrosion failures, examination of the surface profile at the corroded areas can give helpful clues as to what caused the corrosion, and can also reveal any localized features in the microstructure that may have contributed to the problem. Features such as pits, cracks, inclusions and inter-metallic precipitates are identified and characterized using metallographic techniques, and etching is often needed in order to reveal the heat treat condition, as well as potentially deleterious metallic phases. Lower magnifications of up to 100X can be used to characterize overall microstructure uniformity, while higher magnifications of 1,000X to 2,000X can be used to characterize carbide dispersion and appearance. Furthermore, plated parts can be evaluated for plating thickness by examining the surface profile; however, great care must be taken in order to provide good edge retention in specimens that are to be examined along the surface.

Data Review, Conclusions and Recommendations

Once all of the data has been collected, and reviewed, logical conclusions need to be drawn by the analyst. The conclusions must be based on solid engineering principles, and should take into account all of the reported background information, service history and evaluation data. It is imperative that all of the test data be considered during formation of the conclusions, in order to avoid misinterpretation of the results. After the proper conclusions have been reached, the analyst can recommend corrective measures which, if properly followed, should greatly reduce or eliminate the likelihood of future failures. This step involves common sense and sufficient experience on the part of the analyst, in order to avoid unnecessary expenses and, more importantly, the development of other problems. In general, the simplest solution is often the best solution.

3. THE CORROSION PROCESS

It is important to note that corrosion requires three components in order to occur: an anode, a cathode and an electrolyte. The anode usually signifies the corroding component, which is more electrochemically active, while the cathode represents the component that is more electrochemically noble. The electrolyte is the medium through which the corrosion takes place. Any corrosion process requires the anode to be electrically connected to the cathode, in the presence of the electrolyte.

4. RECOGNIZING CORROSION FAILURE MECHANISMS

The features of any corrosion failure give strong clues as to the most likely cause of the corrosion. An understanding of the common corrosion mechanisms will greatly aid in interpreting the features and observations that are revealed in any corrosion investigation. Common corrosion mechanisms include general corrosion, pitting, galvanic corrosion, dealloying, crevice corrosion, microbiologically-influenced corrosion (MIC), corrosion fatigue, stress corrosion cracking (SCC), intergranular corrosion, fretting, erosion corrosion and hydrogen damage.

General Corrosion

When a metal is immersed into an electrolyte, the surface immediately develops millions of microscopic and submicroscopic anodic and cathodic sites. The polarity of an individual site depends on a variety of factors, such as chemical composition, amount of residual stress and microstructure. In general corrosion, the anodic site corrodes, but then develops a protective film that essentially protects the site from further corrosion. In effect, this causes the site to reverse polarity, or become more electrochemically noble than the surrounding sites. In turn, those sites corrode, but immediately develop a protective film. This continuous polarity reversal results in uniform deterioration of the entire exposed surface. This type of corrosion is easily predicted via laboratory testing, and corrosion rates can be directly calculated by weight loss measurements, due to the uniformity of the attack. An aluminum coupon that was partially immersed into 10% hydrofluoric acid exhibited an etched appearance as a result of general corrosion, as shown in Figure 1.

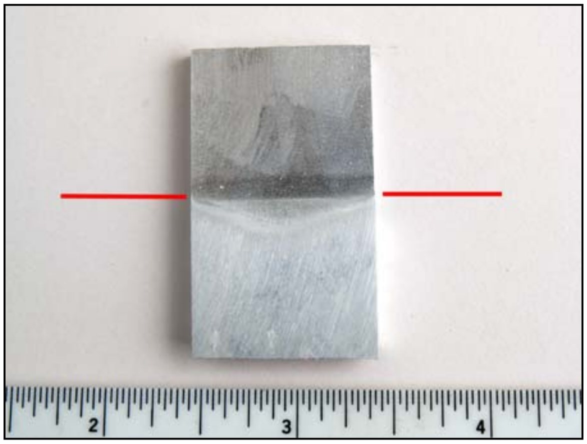

Figure 1 – Partial immersion of an aluminum coupon into 10% hydrofluoric acid produced an etched appearance below the liquid level, which is indicated by the lines.

Pitting

Many metals and alloys have a tendency to form a tenacious passive film on their surfaces, which protects them from general corrosion in certain environments. Pitting occurs when anodic sites develop on the surfaces of such metals, and remain anodic due to the robustness of the protective film in the surrounding areas. Stainless steels, for example, have been found to pit when exposed to chloride-containing substances, particularly under acidic conditions. Pitting can be considered a more serious problem than general corrosion for a few reasons. Firstly, pitting is difficult to predict via laboratory testing. Although some electrochemical test methods have been developed to determine whether various metals are prone to pitting in certain environments, these methods often do not produce results that correlate well to actual components under true service conditions. Secondly, the corrosion rates within the pits tend to be rather high due to localized galvanic effects and acidic conditions; therefore, pits can quickly penetrate through vessel walls and cause leaks without warning. Thirdly, even if pits are detected well before they cause leaks, they can lead to expensive and labor-intensive repairs. Pitted areas often need to be extensively ground in order to completely remove the localized damage caused by the pits, leading to long shutdown periods and expensive repairs. A pitted section of stainless steel is shown in Figure 2.

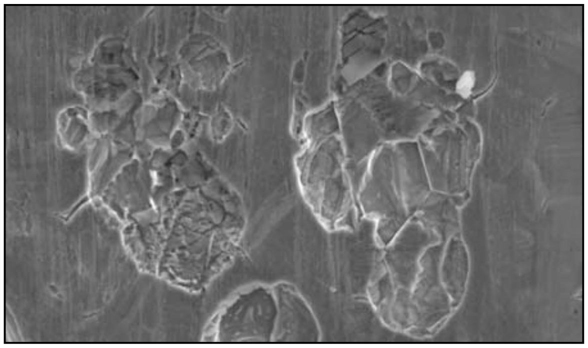

Figure 2 – Scanning electron micrograph showing corrosion pits in a stainless steel trailer skin. (670X)

Galvanic Corrosion

When two dissimilar metals are electrically connected and placed into an electrolyte, the more electrochemically active metal will undergo corrosion at an increased rate, while the more noble metal will be protected to some degree by electrochemical means. It is important to note that moisture from medium- to high-humidity environments alone can serve as the electrolyte; therefore, components may experience galvanic corrosion even if they are not subjected to immersion conditions. Various factors will affect the galvanic corrosion rate in an electrochemical cell, including relative potentials of the dissimilar metals, relative exposed areas of the anode and cathode, electrolyte conductivity, and the polarization tendencies of the metals in the cell. However, prudent design can easily minimize the likelihood of galvanic corrosion in most applications. Selection of appropriate materials, which are relatively close in electrochemical potential, can produce little or no tendency for galvanic corrosion to occur. If significantly dissimilar metals must be used, nonconductive gaskets can be employed to prevent electrical contact between the metals, thereby preventing galvanic corrosion. A metallographic cross section illustrating galvanic corrosion of a weld is shown in Figure 3.

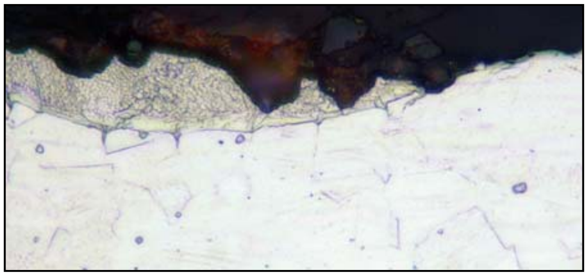

Figure 3 – Metallographic cross section through a stainless steel battery wall, showing localized attack of the weld (top) due to galvanic corrosion. (670X)

Dealloying

Dealloying is a form of galvanic corrosion, which occurs to microscopic phases in metal alloys due to variations in chemical composition, which lead to localized differences in electrochemical potential. Dezincification is a common form of dealloying. Brasses that contain a minimum of 15% zinc are prone to dezincification, where the dissolved zinc is electrochemically more anodic than the surrounding copper. When subjected to adequately corrosive environments, the zinc is leached out of the solid solution and dissolved, leaving behind the pure copper matrix material. Dezincification can be readily recognized in brass components by visual inspection and metallography, as the affected surfaces change color from orange to red. Visual and metallographic features of dezincification are shown in Figures 4 and 5.

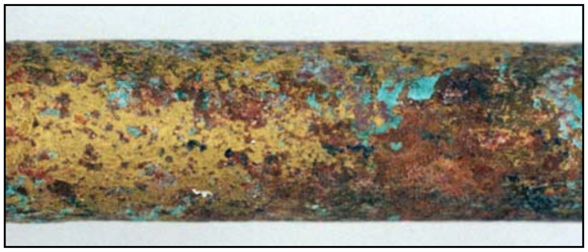

Figure 4 – Dezincification in a free-machining brass had the effect of changing the color from orange to red. (1X)

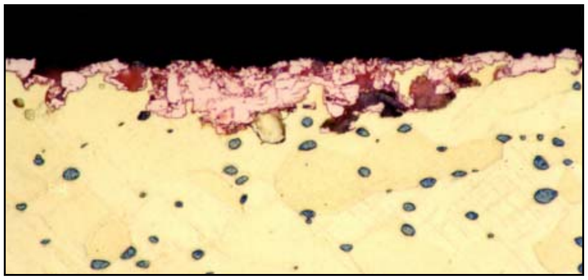

Figure 5 – Metallographic cross section through a free-machining brass showing dezincification along the surface. (670X)

Crevice Corrosion

When crevices are present between a metal surface and another component, the environment within the crevice can differ significantly from the environment in the boldly exposed areas, mostly due to differences in the amounts of available oxygen. The environmental variations effectively alter the localized electrochemical potential, causing the material within the crevice to have a more anodic potential than the material that is exposed to the general environment. Furthermore, the absence of oxygen impairs development of a protective oxide film within the crevice. As a result of these factors, localized corrosive attack occurs to the metal surface within the crevice. A scanning electron micrograph illustrating the effects of crevice corrosion is shown in Figure 6.

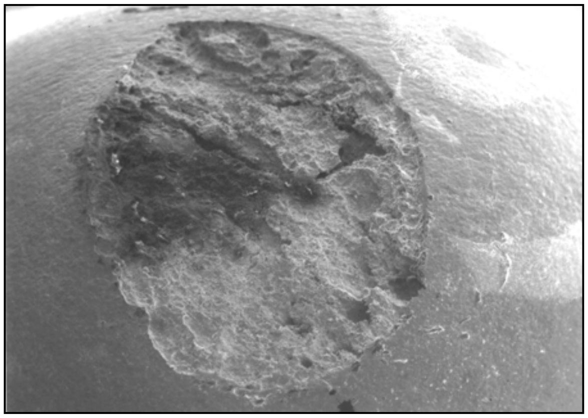

Figure 6 – Scanning electron micrograph showing localized crevice corrosion in a corrugated stainless steel heat exchanger plate. The protrusion was in continuous contact with another plate in the presence of an electrolyte. (13X)

Microbiologically-Influenced Corrosion

Untreated and insufficiently treated water can contain many different types of bacteria, which can lead to microbiologically-influenced corrosion (MIC). This type of corrosion is especially common in stainless steels, although it has been found to occur in carbon steels under some conditions. Under relative slow flow and stagnant conditions, such microbial organisms have a tendency to settle onto metal surfaces and form slime deposits. Once they are attached to the metal surface, they tend to colonize and secrete corrosive substances, which can pit stainless and carbon steels. Anaerobic bacteria, in particular, have a tendency to migrate to low-oxygen environments. As corrosion pits are formed, these organisms prefer the lower-oxygen environments within the pits over the environment in the surrounding areas of the surface. As these organisms concentrate within the pits, they actually form subsurface caverns, which can be easily detected using metallographic techniques. A metallographic cross section showing subsurface caverns from MIC, caused by anaerobic organisms, is presented in Figure 7.

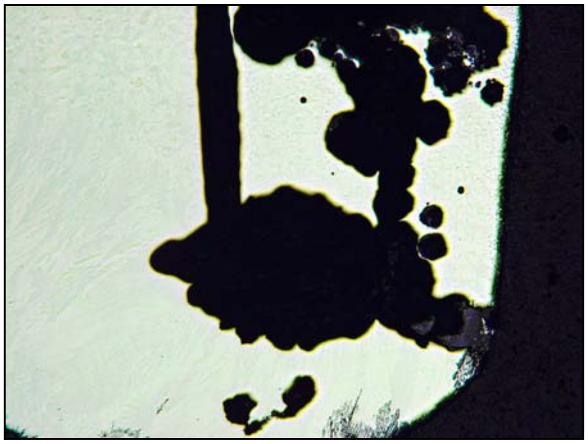

Figure 7 – MIC in stainless steel caused by anaerobic organisms is characterized by subsurface caverns. (33X)

Stress Corrosion Cracking

Passive film-forming metals that are subjected to sustained tensile stress may undergo rapid catastrophic stress corrosion cracking (SCC) while they are exposed to certain mildly corrosive environments. This cracking mechanism is rather rapid, and can thus lead to rapid failures without warning. A variety of materials are susceptible to SCC, including stainless steels, carbon steels, copper alloys, aluminum alloys and titanium alloys. Transgranular SCC commonly occurs in austenitic stainless steels that are subjected to sustained tensile stress and exposed to aqueous chloride-containing substances, particularly steam. SCC is characterized by numerous branched cracks that penetrate deep into the cross section of the material. A metallographic cross section showing such cracks is presented in Figure 8.

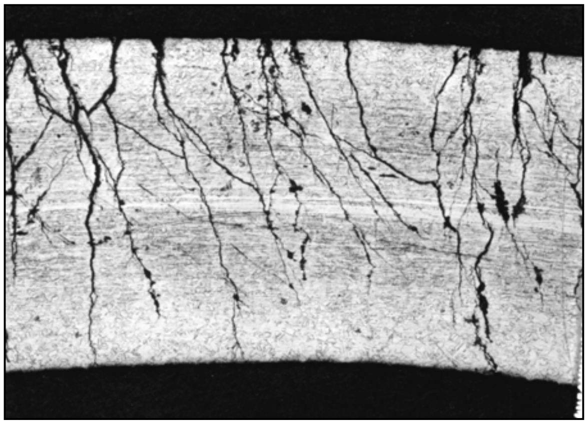

Figure 8 – Transgranular SCC in an austenitic stainless steel is characterized by numerous branched cracks. (21X)

Corrosion Fatigue

Like SCC, corrosion fatigue requires stress and a corrosive environment to occur. However, corrosion fatigue occurs under conditions of cyclic stresses, rather than sustained stress. Corrosion fatigue cracks usually initiate at corrosion pits in the surface, and corrosion occurs to the fractures as they progress. Components that undergo corrosion fatigue often show features that are similar to fatigue fractures, along with severe corrosion of the fracture surface. The crack propagation rate varies with a number of factors, including stress intensity, load frequency, environmental conditions and metallurgy. A cross section through a component that failed via corrosion fatigue is shown in Figure 9.

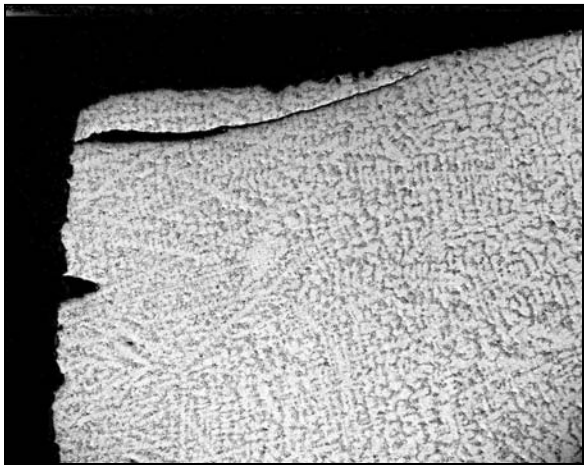

Figure 9 – Metallographic cross section through a cast steel shaft, showing primary and secondary corrosion fatigue cracks (top), in addition to corrosion pits (left). (4X)

Intergranular Attack

Under certain conditions, a metal can undergo intergranular attack (IGA). This phenomenon involves localized corrosion at the grain boundaries, which can result in rapid through-wall corrosion and severe compromise of the material's integrity. One common form of IGA occurs to susceptible austenitic stainless steels that are sensitized. Sensitization of such materials involves heating to temperatures between 950 °F and 1400 °F, and these temperatures are commonly reached during welding. Within this temperature range, carbon will migrate to the grain boundaries and combine with the chromium of the adjacent grains, forming carbides. The chromium-depleted areas along the grain boundaries then become electrochemically more anodic than the material within the bulk grains, leading to rapid corrosion along the grain boundaries. As this corrosion progresses, grains can actually fall out of the microstructure, creating voids. A micrograph showing the effects of IGA on the surface microstructure of a sensitized stainless steel is presented in Figure 10.

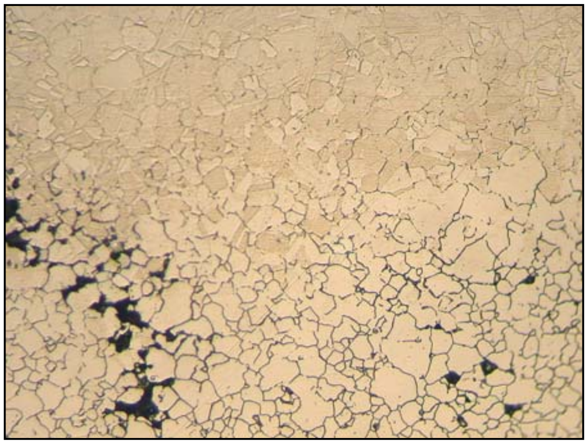

Figure 10 – The surface of a sensitized stainless steel trailer barrel is shown after etching. The sensitized area within the heat-affected zone of a nearby weld is oriented toward the bottom, and shows IGA with evidence of grain fallout. (160X)

Fretting

When two metal surfaces are subjected to vibration and slip while exposed to oxidizing environments, surface damage may occur in the form of fretting. This process involves shearing of the microscopic surface asperities of the mating surfaces, followed by oxidation of the resulting particles. Once oxidized, these particles become abrasive, and cause wear of one or both of the mating surfaces. Fretting can be particularly problematic on sensitive surfaces such as electrical contacts, where sufficient damage can cause intermittent poor contact. A scanning electron micrograph showing an electrical contact surface that underwent fretting is presented in Figure 11.

Figure 11 – Scanning electron micrograph showing fretting damage to an electrical contact in a connector assembly. Fine oxide particles (center) inhibited connection to the mating contact. (330X)

Erosion Corrosion

Virtually all metals are susceptible to erosion corrosion, which is the simultaneous action of erosion (wear) and corrosion. This phenomenon can occur in a variety of environments, but is commonly seen in corrosive liquids containing abrasive particles. In recirculating systems, initial corrosion of components and piping can lead to erosion corrosion as oxide particles are generated. Erosion corrosion has a tendency to produce a wavy appearance to the affected surfaces, as oxides are formed and rapidly removed under turbulent conditions. The inner diameter of a steel tube that underwent severe wall thinning due to erosion corrosion is shown in Figure 12.

Figure 12 – The inner diameter of a steel tube that underwent erosion corrosion from exposure to contaminated water under turbulent flowing conditions shows a wavy morphology with evidence of oxidation. (0.6X)

Hydrogen Damage

Hydrogen can have significantly damaging effects on a variety of metals by causing embrittlement, internal blistering, microstructure damage and even stress corrosion cracking. One form of hydrogen damage is hydrogen embrittlement, which can occur in medium- to high-strength steels. Hydrogen is absorbed by steels during processing steps such as acid pickling and electroplating. If the hydrogen is not sufficiently removed via post-baking, it can lead to delayed but catastrophic failure. Hydrogen embrittlement occurs while the steel component is subjected to sustained tensile stress. The stress can be incurred under tensile, bending and/or torsional loading. As the crystal lattice of the material is stressed, the small hydrogen atoms are free to relocate to grain boundaries in the material. Sufficient amounts of hydrogen will cause severe weakening at the grain boundaries, resulting in sudden brittle fracture. Fractures that resulted from hydrogen embrittlement show distinct features, including an overall intergranular morphology with grain boundary separation, micro-ductility (ductile hairlines) and micropores. A fracture that shows these features is presented in Figure 13.

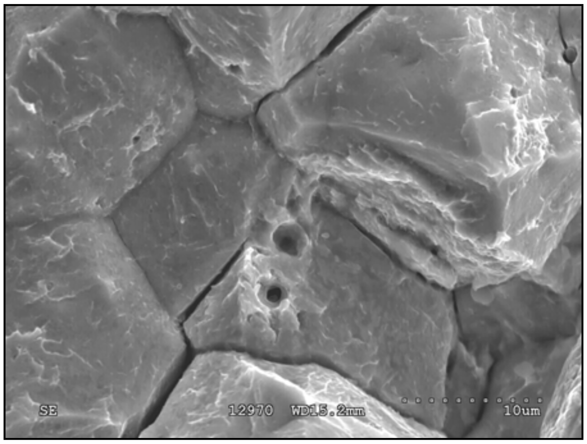

Figure 13 – Scanning electron micrograph showing a brittle fracture through an alloy steel socket head cap screw. The fracture features are characteristic of hydrogen embrittlement. (1,300X)

5. CONCLUSION

Components can fail by a large number of corrosion mechanisms. In any corrosion failure, proper analytical practices and techniques will provide valuable information which, if properly understood, will lead to identification of the failure mode. Once the failure mode has been established, a review of the background history and service conditions will aid in the procurement of sensible corrective measures. Obtaining proper background information and performing the appropriate analyses, combined with an understanding of the material behavior as well as pertinent experience, will produce the best chance of obtaining the accurate conclusions in any failure investigation.

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