

Material Failure Modes, Part III

A Brief Tutorial on Corrosion Related Material Failure Modes

This issue of MaterialEASE is the final installment of a three part series on material failure modes. MaterialEASE 29, published in Volume 9, Number 1 of the AMPTIAC Quarterly, introduced the concept of material failure modes and covered fracture, ductile failure, elastic deformation, creep, and fatigue. MaterialEASE 30, published in Volume 9, Number 2 of the AMPTIAC Quarterly continued the discussion with brief descriptions of impact, spalling, wear, brinelling, thermal shock, and radiation damage. This article completes the series on material failure modes, covering uniform, galvanic, crevice, pitting, intergranular, and erosion corrosion; selective leaching/dealloying; hydrogen damage; stress corrosion cracking; and corrosion fatigue. The three articles taken together make a valuable desk reference for any professional making material selection and design decisions...and that's just what we've done! We have combined these three articles into a desktop reference and placed it on our website for download. Type in the following URL, and download this useful reference guide: <http://amptiac.alionscience.com/deskref>. - Editor

CORROSION

Corrosion is the deterioration of a metal or alloy and its properties due to a chemical or electrochemical reaction with the surrounding environment. The most serious consequence of corrosion is a component or system failure. Failure can occur either by sufficient material property degradation, such that the component or structure is rendered unable to perform its intended function, or by fracture that originates from or is propagated by corrosive effects.

While corrosion manifests itself in many different forms and through various environments and mechanisms, only the most significant forms are discussed in this article. The following sections contain discussions on failures resulting from uniform, galvanic, crevice, pitting, intergranular, and erosion corrosion, selective leaching/dealloying; hydrogen damage; stress corrosion cracking; and corrosion fatigue.

Uniform/General Corrosion

Uniform corrosion is a generalized corrosive attack that occurs over a large surface area of a material (Figure 1). The result is a thinning of the material until failure occurs. Uniform corrosion can also lead to changes in surface properties such as increased surface roughness and friction, which may cause component failure especially in the case of moving parts that require lubricity.

In most cases corrosion is inevitable. Therefore, mitigating its effects or reducing the corrosion rate is essential to ensuring material longevity. Protecting against uniform corrosion can often be accomplished through selection of a material that is best suited for the anticipated environment. The selection of materials for uniform corrosion resistance should simply take into consideration the susceptibility of the metal to the type of environment that will be encountered. Aside from selecting a



Figure 1. Uniform Corrosion on Iron Piping in a Fire Sprinkler System Caused by Leaks in the Threaded Joints. (Photos Courtesy of Corrosion Testing Laboratories, Inc.)[1].

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Table 1. Guidelines for Mitigating Uniform Corrosion.

- Select material that has inherent resistance to corrosion in anticipated operating environment.
- Use barrier coatings (organic or metallic).
- Apply surface treatment to generate uniform oxide layer on surface of metal.
- Use vapor phase inhibitors to deactivate corrosive environment in closed systems (e.g. heat exchanger, boiler, etc.).
- Install cathodic protection system (i.e. impressed current, sacrificial anodes).
- Design system with proper drainage such that there is no standing water.
- Implement routine maintenance schedule to clean/rinse material surfaces.

material that is resistant to uniform corrosion, protection schemes such as barrier coatings can be implemented. Organic or metallic coatings should be used wherever feasible. There are also coatings where additional elements, such as chromium, are incorporated for corrosion resistance. When coatings are not used, surface treatments that artificially produce the metal oxide layer prior to exposure to the environment will result in a more uniform layer with a controlled thickness. A uniform oxide layer can provide effective corrosion resistance for some materials. Also, vapor phase inhibitors may be used in such applications as boilers to adjust the pH level of the environment, thus reducing the rate of corrosion. Table 1 provides a brief list of guidelines that can help minimize uniform corrosion.

Galvanic Corrosion

Galvanic corrosion is a form of corrosive attack that occurs when two dissimilar metals (e.g. stainless steel and magnesium) are electrically connected, either through physically touching each other or through an electrically conducting medium, such as an electrolyte. When this occurs, an electrochemical cell can be established, resulting in an increased rate of oxidation of the more anodic material (lower electrical potential). The opposing metal, the cathode, will consequently receive a boost in its resistance to corrosion. Galvanic corrosion (shown in Figure 2) is usually observed to be greatest near the surface where the two dissimilar metals are in contact.

There are a number of driving forces that influence the occurrence of galvanic corrosion and the rate at which it occurs.



Figure 2. Galvanic Corrosion between a Stainless Steel Screw and Aluminum. A Cathodic Material for Fasteners is Preferred.[2].

Table 2. Guidelines for Mitigating Galvanic Corrosion[3].

- Use one material to fabricate systems or components where practical.
- If mixed metal systems are used, select combinations of metals as close together in the galvanic series as possible, or select metals that are galvanically compatible.
- Avoid the unfavorable area effect of a small anode and large cathode. Small parts or critical components such as fasteners should be the more noble metal.
- Insulate dissimilar metals wherever practical, for example, by using a gasket. It is important to insulate completely if possible.
- Apply coatings with caution. Keep coatings in good repair, particularly the one used on the anodic member.
- Add inhibitors, if possible, to decrease the aggressiveness of the environment.
- Avoid threaded joints for materials far apart in the galvanic series.
- Design for the use of readily replaceable anodic parts or make them thicker for longer life.

Among these influencing factors are the difference in the electrical potentials of the coupled metals, the relative area of each metal, the system geometry, and the environment to which the system is exposed.

In most cases, galvanic corrosion can be easily avoided if proper attention is given to the selection of materials during design of a system. It is often beneficial for performance and operational reasons for a system to utilize more than one type of metal, but this may introduce a potential galvanic corrosion problem. Therefore, sufficient consideration should be given to material selection with regard to the electrical potential differences of the metals. Cathodic protection, electrical insulation, or coatings can also help protect materials from galvanic corrosion. Table 2 provides a brief list of guidelines that can help minimize galvanic corrosion.

Crevice Corrosion

Crevice corrosion occurs as a result of water or other liquids getting trapped in localized stagnant areas creating an enclosed corrosive environment. This commonly occurs under fasteners, gaskets, washers and in joints or in other components with small gaps. Crevice corrosion can also occur under debris built-up on surfaces, sometimes referred to as “poultice corrosion.” Poultice corrosion can be quite severe, due to a gradually increasing acidity in the crevice area.

Several factors including crevice gap width, depth, and the surface ratios of materials affect the severity or rate of crevice corrosion. Tighter gaps, for example, have been known to increase the rate of crevice corrosion of stainless steels in chloride environments. The larger crevice depth and greater surface area of metals will generally increase the rate of corrosion.

Table 3. Guidelines for Mitigating Crevice Corrosion.

- Ensure application is designed to have proper drainage and is absent of areas that can trap moisture and debris.
- Use welded joints instead of mechanical fasteners.
- Select materials that are inherently resistant to corrosion.
- Avoid use of hydrophilic, water absorbing materials.
- Seal gaps and use gap fillers.
- Use and routinely reapply corrosion preventive compounds (e.g. greases and oils).
- Implement a routine maintenance schedule to clean/rinse material surfaces.

Materials typically susceptible to crevice corrosion include aluminum alloys and stainless steels. Titanium alloys normally have good resistance to crevice corrosion. However, they may become susceptible in elevated temperature and acidic environments containing chlorides. Copper alloys can also experience crevice corrosion in seawater environments.

To protect against problems with crevice corrosion, systems should be designed to minimize areas likely to trap moisture, other liquids, or debris. For example, welded joints can be used instead of fastened joints to eliminate a possible crevice. Where crevices are unavoidable, metals with a greater resistance to crevice corrosion in the intended environment should be selected. Avoid the use of hydrophilic materials (strong affinity for water) in fastening systems and gaskets. Crevice areas should be sealed to prevent the ingress of water. Also, a regular cleaning schedule should be implemented to remove any debris build up. Table 3 provides a brief list of guidelines that can help minimize crevice corrosion.

Pitting Corrosion

Pitting corrosion, also simply known as pitting, is an extremely localized form of corrosion that occurs when a corrosive medium attacks a metal at specific points causing small holes or pits to form (Figure 3). This usually happens when a protective coating or oxide film is perforated, due to mechanical damage or chemical degradation (see Figure 4). Pitting can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent, relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight. Failure of a metal due to the effects of pitting corrosion can occur very suddenly. Pitting can have side effects too, for example, cracks may initiate at the edge of a pit due to an increase in the local stress. In addition, pits can coalesce underneath the surface, which can weaken the material considerably.

Among metals and alloys, stainless steels tend to be the most susceptible to pitting corrosion. Polishing the surface of stainless



Figure 3. Corrosion Pit in Grooved Copper Tube (Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

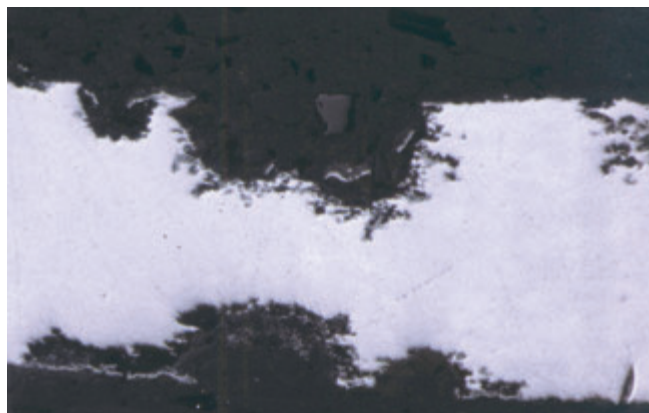


Figure 4. Pitting Corrosion of Copper Radiator Fins under Tin Coating (200X Magnification – Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

steels can increase the resistance to pitting as opposed to etching or grinding the surface. Alloying can have a significant impact on the pitting resistance of stainless steels. Conventional steel has a greater resistance to pitting than stainless steels, but is still susceptible, especially when unprotected. Aluminum in an environment containing chlorides and aluminum brass (Cu-20Zn-2Al) in contaminated or polluted water are usually susceptible to pitting. Titanium is strongly resistant to pitting corrosion.

Proper material selection is very effective in preventing the occurrence of pitting corrosion. Another option for protecting against pitting is to mitigate aggressive environments and environmental components (e.g. chloride ions, low pH, etc.). Inhibitors may sometimes stop pitting corrosion completely. Further efforts during design of the system can aid in preventing pitting corrosion, for example, by eliminating stagnant solutions or by the inclusion of cathodic protection. In some cases, protective coatings can provide an effective solution to the problem of pitting corrosion. However, they can also accelerate the corrosion process at locations where the coating has been breached and the base metal is left exposed to the corrosive environment. Table 4 provides a brief list of guidelines that can help minimize pitting corrosion.

Table 4. Guidelines for Mitigating Pitting Corrosion.

- Select material that is inherently resistant to pitting corrosion.
- Use inhibitors to neutralize corrosive environment in closed systems.
- Eliminate potential build-up of stagnant moisture through proper design.
- Use cathodic or anodic protection.
- Ensure quality application of protective barrier coatings to surface of metal.
- Use surface treatments, such as anodization and conversion coatings, or metal cladding.
- Polish surface to remove surface defects.
- Add alloying elements to metal (e.g. Mo and Cr) for enhanced pitting resistance.

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Intergranular Corrosion

Intergranular corrosion attacks the interior of metals along grain boundaries. It is associated with impurities, which tend to deposit at grain boundaries, and/or a difference in crystallographic phase precipitated at grain boundaries. Heating of some metals can cause a “sensitization” or an increase in the level of inhomogeneity at grain boundaries. Therefore, some heat treatments and weldments can result in a propensity for intergranular corrosion. Some metals may also become sensitized while in operation if



Figure 5. Exfoliation of an Aluminum Alloy in a Marine Environment[2].

used at a high enough temperature to cause such changes in internal crystallographic structure.

Intergranular corrosion can occur in many alloys, but stainless steels, as well as some aluminum and nickel-based alloys, are predominantly susceptible. Stainless steels, especially ferritic stainless steels, have been found to become sensitized, particularly after welding. Aluminum alloys also suffer intergranular attack as a result of precipitates at grain boundaries that are more active. Exfoliation corrosion (shown in Figure 5) is considered a type of intergranular corrosion and occurs in materials that have been mechanically worked to produce elongated grains in one direction. Precipitation of intermetallic phases at grain boundaries can make certain high nickel alloys susceptible. Methods to limit intergranular corrosion are listed in Table 5.

Table 5. Guidelines for Mitigating Intergranular Corrosion.

- Keep impurity levels to a minimum.
- Properly select heat treatments to reduce precipitation at grain boundaries.
- Specifically for stainless steels, reduce the carbon content, and add stabilizing elements (Ti, Nb, Ta) which preferentially form more stable carbides than chromium carbide.

Selective Leaching/Dealloying

Dealloying, also called selective leaching, is a less common form of corrosion where one element is targeted and consequently extracted from a metal alloy, leaving behind an altered structure

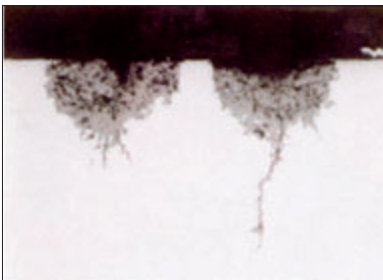


Figure 6. Dezincification of Brass Heat Exchanger Tube (100X Magnification – Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].



Figure 7. Dezincification of Commercial Bronze Wax Actuator from a Water Supply System (Photos Courtesy of Corrosion Testing Laboratories, Inc.)[1].

(Figure 6). The most common form of selective leaching is dezincification (shown in Figure 7), where zinc is extracted from brass or other alloys containing significant zinc content. Left behind are structures that have experienced little or no dimensional change, but whose parent material is weakened, porous and brittle. Dealloying is a dangerous form of corrosion because it can reduce a strong, ductile metal to one that is weak, brittle and subsequently more susceptible to mechanical failure. Since there is little change in the metal’s dimensions, dealloying may go undetected, and failure can occur suddenly. Moreover, the porous structure is open to the penetration of liquids and gases deep into the metal, which can result in further degradation. Selective leaching often occurs in acidic environments.

Reducing the aggressive nature of the atmosphere by removing oxygen and avoiding stagnant solutions and debris buildup can prevent dezincification. Cathodic protection can also be used for prevention. However, the best alternative, economically, may be to use a more resistant material such as red brass, which only contains 15% Zn. Adding tin to brass also provides an improvement in the resistance to dezincification. Additionally, inhibiting elements, such as arsenic, antimony, and phosphorous can be added in small amounts to the metal to provide further improve-

Table 6. Guidelines for Mitigating Selective Leaching.

- Use material that is inherently resistant to selective leaching.
- Some alloying elements for certain metals can improve resistance to selective leaching.
- Avoid stagnant solution/debris buildup.
- Use inhibitors to neutralize corrosive environment.
- Use cathodic protection.
- Avoid using copper with significant zinc content.



Figure 8. Erosion (Cavitation) Corrosion of a Brass Pump Impeller. Air Bubbles Eroded the Soft Copper Oxide Protective Layer Enabling Corrosion of the Base Metal. (Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

ment. Avoiding the use of a copper metal containing a significant amount of zinc altogether may be necessary in systems exposed to severe dezincification environments. Table 6 provides a brief list of guidelines that can help minimize selective leaching.

Erosion Corrosion

Erosion corrosion is a form of attack resulting from the interaction of an electrolytic solution in motion relative to a metal surface. It has typically been associated with small solid particles dispersed within a liquid stream. The fluid motion causes wear and abrasion, increasing rates of corrosion over uniform (non-motion) corrosion under the same conditions. Erosion corrosion is evident in pipelines, cooling systems, valves, boiler systems, propellers, impellers, as well as numerous other components. Specialized types of erosion corrosion occur as a result of impingement and cavitation (Figure 8). Impingement refers to a directional change of the solution, whereby a greater force is exhibited on a surface such as the outside curve of an elbow joint. Cavitation is the phenomenon of collapsing vapor bubbles, which can cause surface damage if they repeatedly hit one particular location on a metal.

There are several factors that influence the resistance of a material to erosion corrosion including hardness, surface smoothness, fluid velocity, fluid density, angle of impact, and the general corrosion resistance of the material to the environment. Materials with higher hardness values typically resist erosion corrosion better than those that have a lower value. There are some design techniques that can be used to limit erosion corrosion. These are listed in Table 7.

Table 7. Guidelines for Mitigating Erosion Corrosion.

- Avoid turbulent flow.
- Add deflector plates where flow impinges on a wall.
- Add plates to protect welded areas from the fluid stream.
- Increase hardness of surface using surface treatment (e.g. shot peening) or hard coating/plating.

Hydrogen Damage

There are a number of different ways that hydrogen can damage metallic materials, resulting from the combined factors of hydrogen and residual or tensile stresses. Hydrogen damage can result in cracking, embrittlement, loss of ductility, blistering and flaking, and microperforation.

Hydrogen induced cracking (HIC) refers to the cracking of a

ductile alloy when under constant stress and where hydrogen gas is present. Hydrogen is absorbed into areas of high triaxial stress producing the observed damage. A related phenomenon, hydrogen embrittlement, is the brittle fracture of a ductile alloy during plastic deformation in a hydrogen gas containing environment. In both cases, a loss of tensile ductility occurs with metals exposed to hydrogen which results in a significant decrease in elongation and reduction in area. It is most often observed in low strength alloys, but also occurs in steels, stainless steels, aluminum alloys, nickel alloys, and titanium alloys.

Another form of damage occurs when high pressure hydrogen attacks carbon and low-alloy steels at high temperatures. The hydrogen will diffuse into the metal and react with carbon resulting in the formation of methane. This in turn results in decarburization of the alloy and possible crack formation. Metal plating operations, for example, can cause hydrogen embrittlement. Methods to deter hydrogen damage are listed in Table 8.

Table 8. Guidelines for Mitigating Hydrogen Damage.

- Limit hydrogen introduced into the metal during processing.
- Limit hydrogen in the operating environment.
- Design structures to reduce stresses (below threshold for subcritical crack growth in a given environment).
- Use barrier coatings.
- Use low hydrogen welding rods.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is an environmentally induced cracking phenomenon (Figure 9) that sometimes occurs when susceptible metals are subjected to a tensile stress and a corrosive environment simultaneously. This is not to be confused with similar phenomena such as hydrogen embrittlement, in which the metal is embrittled by hydrogen, often resulting in the formation of cracks. Moreover, SCC is not defined as the cause of cracking that occurs when the surface of the metal is corroded resulting in the creation of a nucleating point for a crack. Rather, it is a synergistic effort of a corrosive agent and a modest, static stress. Another form of corrosion similar to SCC, although with a subtle difference, is corrosion fatigue. The key difference is that SCC occurs with a static stress, while corrosion fatigue occurs under a dynamic or cyclic stress.

Stress corrosion cracking is a process that takes place within the material, where the cracks propagate through the internal structure, usually leaving the surface unharmed. Aside from an applied



Figure 9. Stress Corrosion Cracking (50X Magnification) in 304L Stainless Steel Pipeline (Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

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Table 9. Guidelines for Mitigating Stress Corrosion Cracking.

- Choose a material that is resistant to SCC.
- Employ proper design features for the anticipated forms of corrosion (e.g. avoid crevices or include drainage holes).
- Minimize stresses including thermal stresses.
- Modify environment (neutralize pH, reduce oxygen content).
- Use surface treatments (shot peening, laser shock peening) which increase the surface resistance to SCC.
- Any barrier coatings will deter SCC as long as it remains intact.
- Reduce exposure of end grains (i.e. end grains can act as initiation sites for cracking because of preferential corrosion and/or a local stress concentration).

mechanical stress, a residual, thermal, or welding stress along with the appropriate corrosive agent may also be sufficient to promote SCC. Pitting corrosion, especially in notch-sensitive metals, has been found to be one cause for the initiation of SCC. SCC is a dangerous form of corrosion because it can be difficult to detect, and it can occur at stress levels which fall within the range that the metal is designed to handle.

Stress corrosion cracking is dependent on environmental factors including temperature, solution, and stress, as well as the metallic structure and composition.[4] However, certain types of alloys are more susceptible to SCC in particular environments, while other alloys are more resistant to that same environment. Increasing the temperature of a system often works to accelerate the rate of SCC. The presence of chlorides or oxygen in the environment can also significantly influence the occurrence and rate of SCC. There are several methods that may be used to minimize the risk of SCC. Some of these methods are listed in Table 9.

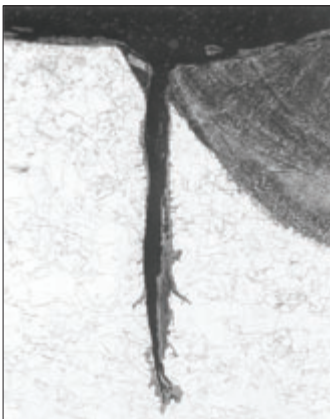


Figure 10. Corrosion Fatigue Crack (60X Magnification) Adjacent to a Weld in 316 Stainless Steel (Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

considered to be a subset of stress corrosion cracking, but the fracture mechanics and methods of prevention deviate enough from those of SCC that it warrants a separate discussion. Furthermore, SCC occurs under static stress while corrosion fatigue occurs under a cyclic stress (part of which is tensile stress).

Corrosion fatigue is a potential cause for the failure of many types of metals and alloys in various types of environments.

Corrosion Fatigue

Corrosion fatigue is the environmentally-assisted mechanical degradation of a material due to the combined effects of corrosion and fatigue (a direct result of cyclic stress loading). This corrosion mode is shown in Figure 10. It is often

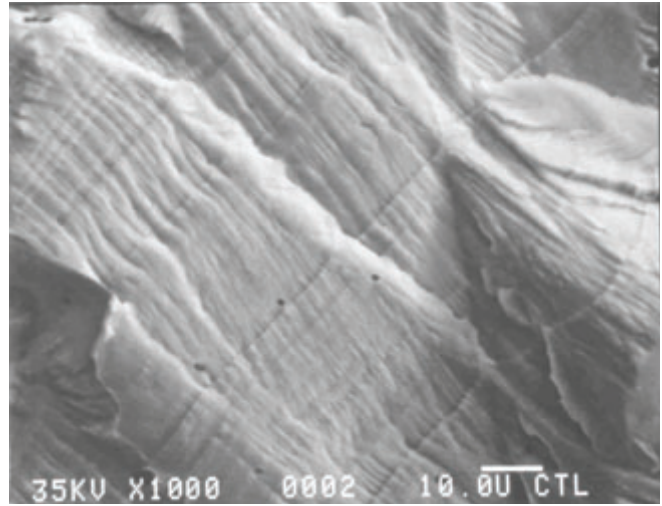


Figure 11. Fatigue Striations Observed with Scanning Electron Microscope (1000X Magnification – Photo Courtesy of Corrosion Testing Laboratories, Inc.)[1].

Materials that experience corrosion fatigue essentially exhibit a decrease in fatigue strength due to the effects of electrochemical degradation (corrosive environment). The stress required for both crack initiation and propagation is lower in corrosive environments. The crack growth rate can be much higher in a corrosive environment than it is in a non-corrosive environment. Therefore, the fatigue life of a material is shortened if it is simultaneously exposed to a corrosive environment and fatigue conditions. Like the general case of fatigue, corrosion fatigue cracking is often characterized by “beach marks” or striation patterns (shown in Figure 11), which are perpendicular to the crack propagation direction.

There are a number of factors that affect the onset of corrosion fatigue and the growth rate of cracks caused by this form of corrosion. For example, corrosion damage, such as pitting, causes stress raisers in the vicinity of the pit, much like notch

Table 10. Guidelines for Mitigating Corrosion Fatigue.

- Polish surface to make material more resistant to crack initiation.
- Limit operating temperatures.
- Reapply coatings or corrosion preventive compounds in damaged areas.
- Employ designs which minimize stresses to the components.
- Choose heat treatments that reduce residual stresses.
- Use surface treatments that enhance corrosion fatigue resistance, such as shot peening or laser peening.
- Use inhibitors and barrier coatings to block corrosive species from the metal.
- Reduce hydrogen contamination during fabrication, heat treatment or manufacturing.
- Select materials that are not sensitive to corrosion fatigue.

effects. This can lead to crack initiation at a stress below that for a material in a non-corrosive environment. The crack will then propagate at a faster rate, as corrosive elements enter the crack. Temperature, metal composition, strength and fracture toughness are other examples of environmental and material factors that affect the occurrence and rate of corrosion fatigue.

Similar to preventing stress corrosion cracking, material selection is very important in corrosion fatigue prevention. Fracture toughness and strength are both important material properties when considering how to protect against corrosion fatigue. Other methods to deter corrosion fatigue are listed in Table 10.

CONCLUSION

Corrosion is a widespread and costly problem. While some of the damage it causes is simply cosmetic, several corrosion modes can cause catastrophic failure before they are even identified as a problem. Therefore, for critical components and systems, it is very important to understand the various forms of corrosion failure that were discussed in this article. Material selection during system or component design is the first step in preventing a catastrophic corrosion problem.

The three-part series of articles on material failure modes presented in this and the previous two issues of the *AMPTIAC Quarterly* has covered the most common and significant failure mechanisms. However, there is another entire field related to system failure, and that is electronic failure. For many systems, electronic failure is significant and should be considered during the design phase of a system or component.

ACKNOWLEDGEMENT

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