

Microbiologically Influenced Corrosion

A Bigger Problem than you think!

Material Failure Modes

Materia

DARP4

Comparing Environmentally-assisted Cracking Forms



AMPTIAC is a DOD Information Analysis Center Administered by the Defense Technical Information Center

Editorial: Failure is an Integral Part of Success

It was some years ago when I first heard that expression – I've long since forgotten where or when I heard it, so my apologies to its originator. It's not an intuitive axiom, but with time and experience, I have come to see the wisdom of it. This may seem an alien concept to some, particularly in this country, where we pride ourselves on being success-driven and intolerant of failure. It's not too hard to find quotes on the topic from numerous famous Americans, such as Benjamin Franklin, George S. Patton, or even Donald Trump. My own favorite quote follows:

"Failure is not an option" - these are the now-immortal words of Gene Kranz, the flight director of the Apollo 13 moon mission, when faced with the seemingly impossible task of bringing home alive three astronauts before their dying spacecraft had completely run out of power and the life-giving oxygen needed to sustain them. Through this declaration, Kranz had laid down a challenge to the hundreds of ground personnel supporting the mission: find a way. Kranz's team rose to the task; exceeding the constraints of design and surpassing the limits of their own imaginations. The mission was called "A Successful Failure," in that while the primary mission objective (landing on the moon) was not met, the greater goal of returning the crew safely to the earth was, in spite of the odds. It was the specter of failure (and all that it represented) that drove NASA professionals to transcend conventional wisdom and practices to bring the Apollo 13 crew home. However, while the basic philosophy of the Kranz doctrine is noble, it is not an accurate portrayal of failure - at least not in an engineering sense. In fact, the term failure has many different and even conflicting connotations, depending largely on one's perspective. It is this concept of failure and its role in engineering design that I wish to examine further.

When it comes to any material or manmade structure, not only is failure not an option, it is an inevitability! The universe's predisposition towards entropy (as stated by the second law of thermodynamics) can be a pesky and unforgiving master. It dictates that highly-ordered matter (such as any industrially fabricated material) degrades to lower-energy, more-disordered states. This is why metal rusts, radioactive elements decay, and paper disintegrates – they are all degrading to more fundamental (and functionally useless) base states. Whether that degradation takes place in a fraction of a second or over eons, its ultimate outcome is the same – all materials are predestined to fail given sufficient time.

As luck would have it, all three articles in this issue of the AMPTIAC Quarterly deal with one aspect of material failure or another, thus some commentary on the topic seemed timely. At present, there are over forty recognized mechanisms of material failure, ranging from the ordinary, like simple buckling or yielding to more exotic mechanisms like radiation damage or selective leaching. While nature dictates that failure cannot ultimately be avoided, it can be delayed, deferred, or altered by sound design and material selection practices. Understanding a system's likely service environment allows engineers to identify potential failure mechanisms during the design cycle; and thus make the strategic material and design decisions to prevent premature component failures and out-of-cycle sustainment activities. In this way, failure is not the antithesis of success, but a guidepost on the path to it. It is only by being mindful of the limitations imposed by failure mechanisms on our palette of material choices that we can design and build robust systems that will reward the DOD's acquisition investments with high rates of readiness and maximal service lives.

Lastly, this issue marks another transition in the evolution of the *Quarterly*, as it represents a changing of the guard. As my responsibilities in AMPTIAC have evolved, it is now time to pass the mantle of the editor's post to another member of our staff, Mr. Benjamin Craig. Ben has been a contributor to the *Quarterly* for several years and has become a staple of the operation. I am confident he will bring new blood and fresh ideas to one of AMPTIAC's most successful enterprises. I would encourage all of you to give Ben the same support and encouragement that you have afforded me over these past several years.

My sincerest thanks,

Chris Grethlein Deputy Director, AMPTIAC

About the cover: Sulfate reducing bacteria (SRB) often contribute to microbiologically influenced corrosion of metals. This type of bacteria forms biofilms (blue regions in the image), and in this case caused the production of sulfide ions that bonded to metallic zinc to form zinc sulfide particles (green areas), which then aggregated to form spherical clumps (yellow spheres). Image reprinted with permission from "Formation of Sphalerite (ZnS) Deposits in Natural Biofilms of Sulfate-Reducing Bacteria," M. Labrenz et.al., Science, Vol. 290, No. 5497, Dec. 2000, pp.1744-1747. ©Copyright 2000, AAAS.

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Under the Microscope: Understanding, Detecting, and Preventing Microbiologically Influenced Corrosion

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INTRODUCTION

A renewed interest in corrosion prevention and control has resulted in a major push within the DOD to help bring down the Department's enormous maintenance costs attributed to corrosion. Much of these rising costs can be directly attributed to extending the useful life of systems well beyond their original specifications. However, one type of corrosion that can produce unexpected problems, premature failures, and costly repairs is microbiologically influenced corrosion (MIC). Microorganisms have long been known to influence corrosion, causing throughwall corrosion of piping and heat exchanger tubes 10-1000 times faster than normal.[1] Effective prevention and control of MIC involves an underlying knowledge of the microorganisms responsible for increased corrosion rates as well as methods that can be implemented to detect and prevent microbial growth.

MIC is not a form of corrosion, but rather is a process that can influence and even initiate corrosion. It can accelerate most forms of corrosion; including uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, intergranular corrosion, dealloying, and stress corrosion cracking. In fact, if unfamiliar with MIC, some corrosion problems may be misdiagnosed as conventional chloride-induced corrosion. One prominent indicator of MIC is a higher rate of attack than one would normally expect. MIC can affect numerous systems, and can be found virtually anyplace where aqueous environments exist. It is not exclusive to water-based systems, as it occurs in fuel and lubrication systems as well. Table 1 lists applications where MIC has been found to be prominent while Figure 1 shows one such location.

TYPES OF MICROORGANISMS

The types of microorganisms with species attributable to MIC include algae, fungi, and bacteria.[3] Algae can be found in most any aquatic environment ranging from freshwater to concentrated salt water. They produce oxygen in the presence of light (photosynthesis) and consume oxygen in darkness. The availability of oxygen has been found to be a major factor in corrosion of metals in saltwater environments. Algae flourish in temperatures of 32 - 104°F and pH levels of 5.5 - 9.0. Fungi consist of mycelium structures, which are an outgrowth of a single cell or spore. Mycelia are immobile, and can grow to reach macroscopic dimensions. Fungi are most often found in soils, although some species are capable of living in water environments. They metabolize organic matter, producing organic acids.

Pipelines/storage tanks (water, wastewater, gas, oil)	Stagnant areas in the interiorExterior of buried pipelines and tanks,	 Aerobic and anaerobic acid producers Sulfate reducing bacteria
	especially in wet clay environments	 Suitate reaucing bacteria Iron/manganese oxidizing bacteria Sulfur oxidizing bacteria
Cooling systems	Cooling towersHeat exchangersStorage tanks	 Aerobic and anaerobic bacteria Metal oxidizing bacteria Slime forming bacteria Algae Fungi
Docks, piers, and other aquatic structures	Splash zoneJust below low tide	Sulfate reducing bacteria
Vehicle fuel tanks	Stagnant areas	• Fungi
Power generation plants	Heat exchangersCondensers	 Aerobic and anaerobic bacteria Sulfate reducing bacteria Metal oxidizing bacteria
Fire sprinkler systems	Stagnant areas	Anaerobic bacteriaSulfate reducing bacteria

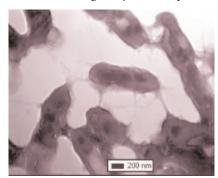


Figure 1. Interior of a Ballast Tank on a Navy Ship[4].

Bacteria are generally classified by their affinity to oxygen. *Aerobic* species require oxygen to carry out their metabolic functions, while *anaerobic* species do not live or metabolize in the presence of oxygen. Facultative bacteria can grow in either environment, although they prefer aerobic conditions. Microaerophilic bacteria require low concentrations of oxygen. Oddly enough, aerobic and anaerobic organisms have often been found to co-exist in the same location. This is because aerobic species deplete the immediate surroundings of oxygen creating an ideal environment

for anaerobes. Bacteria are further classified by shape into spherical (bacillus), rod (coccus), comma (vibrio), and filamentous (myces) species. Figure 2 is an example of rod-shaped bacteria observed using transmission electron microscopy.

Microorganisms in the planktonic state refer to those organisms floating freely in the aqueous environment or in air. They



can resist harsh chemicals including acids, alcohols, and disinfectants, and can withstand drying, freezing, and boiling conditions.[6] Some spores have the ability to last hundreds of years and then germinate once favorable conditions exist. Microorganisms in the sessile state are those that have attached themselves

Figure 2. Rod-Shaped Pseudomonas Bacteria[5].

to a surface and have developed a protective membrane, collectively called a biofilm. Microorganisms have the ability to reproduce quickly; some doubling in as little as 18 minutes. When left untreated, they can rapidly colonize in stagnant aqueous environments, potentially introducing a highly active corrosion cell.

MICROORGANISMS THAT ACCELERATE CORROSION

Once a microorganism forms a biofilm on a material's surface, a microenvironment is created that is dramatically different from the bulk surroundings. Changes in pH, dissolved oxygen, and organic and inorganic compounds in the microenvironment can lead to electrochemical reactions which increase corrosion rates. Microorganisms may also produce hydrogen, which can cause damage in metals. Most microorganisms form an extracellular membrane which protects the organism from toxic chemicals and allows nutrients to filter through.[6] Biofilms are resistant to many chemicals by virtue of their protective membrane and ability to breakdown numerous compounds. They are significantly more resistant to biocides (chemicals used to kill microorganisms) than planktonic organisms. Some bacteria even metabolize corrosion inhibitors, such as aliphatic amines and nitrites, decreasing the inhibitor's ability to control corrosion. Microorganisms' metabolic reactions attributable to metallic corrosion involve sulfide production, acid production, ammonia

production, metal deposition, and metal oxidation and reduction. Several groups of microorganisms have been attributed to MIC, and are described briefly below.[7] Following these recognized forms, Table 2 then lists some specific microorganisms within these categories, along with their characteristics.

Sulfate Reducing Bacteria

Sulfate reducing bacteria (SRB) are anaerobic microorganisms that have been found to be involved with numerous MIC problems affecting a variety of systems and alloys. They can survive in an aerobic environment for a period of time until finding a compatible environment. SRB (see Figure 3) chemically reduce sulfates to sulfides, producing compounds such as hydrogen sulfide (H₂S), or iron sulfide (Fe₂S) in the case of ferrous metals. The most common strains exist in the temperature range of 25 - 35°C, although there are some that can function at temperatures of 60°C. They can be detected through the presence of black precipitates in the liquid media or surface deposits, as well as a characteristic hydrogen sulfide smell.



Figure 3. Biofilms (Blue) Produced by SRB Cause the Formation of ZnS (Green) and ZnS Aggregates (Yellow) from Metallic Zinc.[8] ©2000 AAS. Reprinted with Permission.

Sulfur/Sulfide Oxidizing Bacteria

Sulfide oxidizing bacteria (SOB) are an aerobic species which oxidize sulfide or elemental sulfur into sulfates. Some species oxidize sulfur into sulfuric acid (H_2SO_4) leading to a highly acidic (pH \leq 1) microenvironment. The high acidity has been associated with the degradation of coating materials in a number of applications. They are primarily found in mineral deposits and are common in wastewater systems. SRB are often found in conjunction with SOB.

Iron/Manganese Oxidizing Bacteria

Iron and manganese oxidizing bacteria have been found in conjunction with MIC, and are typically located in corrosion pits on steels. Some species are known to accumulate iron or

manganese compounds resulting from the oxidation process. High concentrations of manganese in biofilms have been attributed to the corrosion of ferrous alloys, including pitting of stainless steels in treated water systems. Iron tubercles have also been observed to form as a result of the oxidation process (Figure 4).



Figure 4. Tubercles as a Result of MIC (Courtesy of Metallurgical Technologies, Inc.) [9].

Slime Forming Bacteria

Slime forming bacteria are aerobic organisms which develop polysaccharide "slime" on the exterior of their cells. The slime

controls permeation of nutrients to the cells and may breakdown various substances, including biocides. Slime formers have been responsible for the decreased performance of heat exchangers as well as clogging of fuel lines and filters. They can prevent oxygen from reaching the underlying metal surface, creating an environment suitable for anaerobic organisms.

Organic Acid Producing Bacteria

Some anaerobic organisms also produce organic acids. These bacteria are more apt to be found in closed systems including gas transmission lines and sometimes closed water systems.

Acid Producing Fungi

Some fungi produce organic acids which attack iron and aluminum alloys. Similar to slime formers, they can create environments suitable for anaerobic species. The widespread corrosion problems observed in aluminum fuel tanks in aircraft have been attributed to these organisms.

MIC IN METALS

Since MIC is a mechanism that accelerates corrosion, it should be expected to occur more often in metal alloys with susceptibilities to the various forms of corrosion, and in environments conducive to biological activity. Metals used in the applications listed in Table 1 include mild steels, stainless steels, copper alloys, nickel alloys and titanium alloys. In general, mild steels can exhibit everything from uniform corrosion to environmentally-assisted cracking, while the remaining alloys usually only show localized forms. Mild steels, stainless steels, aluminum, copper, and nickel alloys have all been shown to be susceptible to MIC, while titanium alloys have been found to be virtually resistant to MIC under ambient conditions.

Mild Steels

MIC problems have been widely documented in piping systems, storage tanks, cooling towers, and aquatic structures. Mild steels are widely used in these applications due to their low cost, but are some of the most readily corroded metals. Mild steels are

Table 2. Common	Microorganisms Fou	und in Conjunction with	Microbiologically Influence	d Corrosion[10].
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	Genus or Species	рΗ	Temperature (°F)	Oxygen Requirement	Metals Affected	Metabolic Process
	Desulfovibrio	4-8	50-105	Anaerobic	Iron and steel, stainless steels, aluminum, zinc, copper alloys	Use hydrogen in reducing SO ₄ ^{2.} to S ^{2.} and H ₂ S; promote formation of sulfide films
-	Desulfotomaculum	6-8	50-105 (some at 115-165)	Anaerobic	Iron and steel, stainless steels	Reduce SO ₄ ²⁻ to S ²⁻ and H ₂ S
	Desulfomonas	-	50-105	Anaerobic	Iron and steel	Reduce SO ₄ ²⁻ to S ²⁻ and H ₂ S.
-	Acidithiobacillus thiooxidans	0.5-8	50-105	Aerobic	Iron and steel, copper alloys, concrete	Oxidizes sulfur and sulfides to form H ₂ SO ₄ ; damages protective coatings
-	Acidithiobacillus ferrooxidans	1-7	50-105	Aerobic	Iron and steel	Oxidizes ferrous (Fe ²⁺) ions to ferric (Fe ³⁺) ions
Bacteria	Gallionella	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ion: and manganous (Mn ²⁺) to manganic (Mn ³⁺) ions; promotes tubercule formation
-	Siderocapsa	-		Microaerophilic	Iron and carbon steel	Oxidizes iron
	Leptothrix	6.5-9	50-95	Aerobic	Iron and steel	Oxidizes ferrous to ferric ions and manganous to manganic ions
	Sphaerotilus	7-10	70-105	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous to ferric ions and manganous to manganic ions; promotes tubercule formation
	Sphaerotilus natans	-	-	-	Aluminum alloys	-
	Pseudomonas	4-9	70-105	Aerobic	Iron and steel, stainless steels	Some strains reduce Fe ³⁺ to Fe ²⁺
	Pseudomonas aeruginosa	4-8	70-105	Aerobic	Aluminum alloys	-
Fungi	Cladosporium resinae	3-7	50-115 (best at 85-95)		Aluminum alloys	Produces organic acids wher metabolizing certain fuel constituents

normally coated for corrosion protection, while cathodic protection may also be used for select applications. Galvanization (zinc coating) is commonly used to protect steel in atmospheric environments. Bituminous coal tar and asphalt dip coatings are often used on the exterior of buried pipelines and tanks, while polymeric coatings are used for atmospheric and water environments. However, biofilms tend to form at flaws in the coating surfaces. Furthermore, acid producing microorganisms have been found to dissolve zinc and some polymeric coatings.[11] Numerous cases have also been documented where microorganisms caused debonding of coatings from the underlying metal. Delamination of the coating, in turn, creates an ideal environment for further microbial growth.

Poor quality water systems and components with areas that accumulate stagnant water and debris are prone to MIC. In some extreme cases, untreated water left stagnant within mild steel piping has caused uniform corrosion throughout the low lying areas. This has been seen to occur in underground pipes that have been left unused for periods of time.[11] Many power plant piping failures have been found to be the result of introducing untreated water into a system. SRB has been the primary culprit in such cases. A change to a more corrosion resistant material is not always the most appropriate answer when it comes to solving MIC problems. For example, an upgrade from carbon steel to stainless steel in a nuclear power plant caused a change in MIC problems, that in some instances were even more severe. SRB has also been found in conjunction with underdeposit corrosion occurring in cooling towers. Wet soils containing clay have played a major role in the occurrence of underground MIC problems. Under such conditions, the exterior of underground piping and storage tanks have experienced coating delamination and corrosion as a result of biofilm growth.

Stainless Steels

Stainless steels have suffered MIC problems under the same sets of conditions as mild steels - primarily in situations where water accumulates. There are two notable problems that have surfaced with MIC of stainless steel. First, stainless steels corrode at an accelerated rate, primarily through pitting or crevice corrosion, which occurs in low lying areas, joints, and at corner locations. This has been found to occur in tanks and piping systems that were hydrotested* using well water, and then put in storage before service without using biocides or drying the system to prevent microbial growth.[11] In one particular case, a 304 stainless steel pipeline for freshwater service, failed 15 months after being hydrotested.[12] The second MIC problem discovered with stainless steels is that corrosion occurs adjacent to weldments. Microorganisms readily attack areas around welds due to the inhomogeneous nature of the metal. In one case, perforation occurred adjacent to a welded seam in a 0.2 inch diameter 316L stainless steel pipe after being in service for four months under intermittent flow conditions.[13] Stainless steels containing 6% molybdenum or greater, have been found to be virtually resistant to MIC.[11]

Aluminum Alloys

The major applications where MIC has attacked aluminum alloys have been in fuel storage tanks and aircraft fuel tanks. [11] MIC problems typically occur in the low-lying areas of the tanks and at water-fuel interfaces. Contaminants in fuels, such as surfactants and water soluble salts, have largely contributed to the formation of biofilms in these systems. Fungi and bacteria have been found to be the main culprits. Corrosion of aircraft fuel tanks has been widely attributed to *Cladosporium resinae*, a fungus. Its presence decreases the pH to approximately 3-4, which can harm the protective coatings and underlying metal. The *pseudomonas aeruginosa* species is also known to be connected with MIC of aluminum fuel tanks.

Additionally, heavy fungal growth on interior surfaces of helicopters has occurred after undergoing depot maintenance.[14] Fungal growth had been reported in passenger areas of the H-53 helicopter before being returned to field use and as a result it was slated for cleaning. Fungi could be found on virtually all interior surfaces of the helicopter. The surfaces were cleaned with 100% isopropanol, treated with a biocide, and followed by application of a corrosion preventive compound. The procedure removed most of the microorganisms present and was effective at killing spores. However, some biofilms remained, which rapidly reproduced before the aircraft was even returned to service.

Copper Alloys

Copper alloys find use in seawater piping systems and heat exchangers, which are susceptible to MIC. Microbial products that can be harmful to copper alloys include carbon dioxide (CO₂), hydrogen sulfide (H₂S), ammonia (NH₃), organic and inorganic acids, and other sulfides.[11] MIC observed in copper alloys includes pitting corrosion, dealloying and stress corrosion cracking. Higher alloying content in copper usually results in a lower corrosion resistance. Although MIC has been found in both, more problems have been documented with 70/30 than with 90/10 Cu/Ni alloys. MIC has also been documented in Admiralty brass (Cu-30Zn-1Sn), aluminum brass (Cu-20Zn-2Al), and aluminum bronze (Cu-7Al-2.5Fe). Ammonia and sulfides have gained considerable attention as compounds that are corrosive to copper alloys. Admiralty brass tubes have been found to suffer stress corrosion cracking in the presence of ammonia. Seawater that is high in sulfide content, has caused pitting and stress corrosion cracking in copper alloys. SRB has also been known to attack copper alloys causing dealloying of nickel or zinc in some cases.

Nickel Alloys

Nickel alloys are often used for applications subject to high velocity water environments, including evaporators, heat exchangers, pumps, valves, and turbine blades, as they generally have a higher resistance to erosive wear than copper alloys.[11] However, some nickel alloys are susceptible to pitting and crevice corrosion under stagnant water conditions, so that downtime and static periods can lead to potential MIC problems. Monel 400 (66.5Ni-31.5Cu-1.25Fe) has been found to be susceptible to underdeposit MIC. Pitting corrosion, intergranular corrosion, and dealloying of nickel have all been observed with this alloy in the presence of SRB. Ni-Cr alloys have been found to be generally resistant to MIC.

MONITORING/DETECTION METHODS

Early detection of potential MIC is crucial to the prevention of equipment failure and extensive maintenance. The most

common detection methods involve sampling bulk liquids from within the system and monitoring physical, chemical, and biological characteristics. The goal is to identify favorable conditions for biofilm formation and growth, so that the internal environment may be adjusted appropriately. Visual inspections of accessible areas should also be performed on a routine basis. Additional methods that may be utilized include coupon monitoring, electrochemical sensor and biosensor techniques.



Monitoring equipment is available for measuring a number of properties of the bulk system. A common practice has been to directly monitor temperature, pH, conductivity, and total dissolved solids, while taking samples to evaluate (by portable or laboratory testing methods) dissolved

Figure 5. Bacteria Culture[15].

gases and bacteria counts, and to identify bacteria.[2] Bacteria counting, via cultured growth, may be helpful, but strict conditions must be set to produce meaningful results. The most important factor in bacterial counts is observing changes in trends rather than in actual numbers. Consistency is crucial where deviations in sample location, temperature, growing media, growth time, and even changes in technicians can affect the results. A strict schedule must also be maintained. Changes in bacteria counts are used to adjust biocide usage, and may also be indicative of biofilm growth in the case of differences in counts across a system. Bacteria cultures can also be used to identify specific species present (Figure 5). Direct bacteria counts can be performed using a microscope to inspect bacte-



Figure 6. Inspection of Bacteria on a Stained Microscope Slide[16].

ria which have been placed onto a slide and may also be stained for viewing, as shown in Figure 6. Visual inspections should be performed on exposed surfaces where algae and fungal growth can occur and on surfaces exposed during maintenance procedures. The presence of SRB can be detected by observing black particles in the liquid media and/or deposited on surfaces (a result of iron sulfide and/or copper sulfide formation), or by a distinct hydrogen sulfide odor.[17] Fluorescent dyes can be used to enhance visual detection, as biofilms absorb some of the dye, whereby an ultraviolet light is then used to expose the microorganisms.

Coupons have been found to be quite useful in detecting MIC, especially when used in conjunction with additional monitoring techniques. Coupons are small metal samples placed within the system and periodically extracted to measure corrosion rates by a weight loss method and possibly to collect microorganisms from biofilms present on the coupon for identification. Proper placement of the coupons within the system plays a key role in MIC monitoring and detection. Coupons should be placed in locations where MIC is likely to occur. Electrochemical sensing techniques, such as electrical impedance spectroscopy and electrochemical noise, are other means of detecting MIC. Electrochemical sensors detect characteristics of corrosion reactions, such as changes in electrical conductivity. As with coupons, strategic placement of the sensors in the systems is crucial to detecting MIC.

One type of sensor designed specifically for biofilm detection uses a probe that attracts microbial growth.[1] Utilizing knowledge of the electrochemical conditions under which biofilms occur, probes have been developed that replicate these preferred conditions. The sensor then alerts operators when biofilm activity is present. Sensors should ideally be placed in areas where biofilm growth is more likely. Another method that may be used specifically to detect microorganisms in water systems is the use of fluorogenic bioreporters.[18] These are compounds (dyes) that experience a change in their fluorescence upon interaction with microorganisms. Activity is determined by the ratio of fluorescence of the reacted dye, extracted from the system or measured in-service, to the unreacted dye. The ratio increases with biological activity and can be used to effectively regulate the use of biocides. This method however, does not distinguish between planktonic and sessile organisms. Thus, problems could be growing in the system without being detected.

MITIGATION METHODS

Clearly, the best way to prevent MIC is to prevent the growth of biofilms altogether. Once a biofilm has formed, it is more resistant to biocides, and can rapidly grow if not completely removed. The emphasis is placed on cleanliness and incorporating established corrosion prevention and control techniques for the various metals and forms of corrosion. Monitoring and detection of microorganisms will effectively guide preventive maintenance procedures.

Maintaining the cleanliness of systems involves monitoring the quality of water, fuel, or lubricants present in the system. This includes water content in fuel and lubrication systems. Water content should be monitored and removed when it becomes too high. All fluids should be monitored for solid particles and filtered to prevent particle contamination. Contaminants increase the likelihood of biofilms, as they can sometimes be used as nutrients. Bacterial counts and biosensing provide information that can help adjust the level of biocides introduced to the system to an optimal concentration. Biocides are widely used and are effective at killing planktonic microorganisms. The cost of biocides is significant however, and they are also quite toxic. Effectively managing their use can reduce costs and minimize the damaging effects on the environment. Preventive maintenance also includes scheduled cleaning of exterior components where any debris accumulation has occurred. Non-abrasive cleaning methods are preferred so as to not damage coatings. Inspection/cleaning should also be performed on normally inaccessible components that are exposed during maintenance and repair activities. Designing systems that minimize MIC prone areas and providing accessibility for maintenance helps to promote system cleanliness. This involves eliminating stagnant and low-flow areas, minimizing crevices and welds, incorporating filtration, drains, and access ports for treatments, monitoring/sampling, and cleaning.

Established corrosion prevention and control methods that are employed to protect metals from the various forms of corrosion will also help mitigate MIC. This includes designing systems to minimize stagnant water conditions, proper base material and coating selection, cathodic protection, sealing crevices and around fasteners, using gaskets to minimize galvanic corrosion, proper heat treatments, and post weld treatments. For underground structures, providing ample drainage by backfilling with gravel or sand will help prevent MIC. In some cases, a change to an alternate material such as PVC piping has greatly reduced underground pipeline corrosion problems. Coatings can be formulated with biocides, though such coatings are not generally used on the interior of systems. Smooth surface finishes with minimized defects are preferred. Research into alternative coatings that may deter MIC has shown polydimethylsiloxane coated 4340 steel to have favorable results.[19] The silicone compounds significantly reduced MIC of the steel in a 0.6M NaCl solution over a two year period.

SUMMARY

The prevention and control of MIC may seem like a daunting task. However, with knowledge of how and where MIC occurs, as well as the prevention and control methods that may be used, a majority of problems can be prevented. Maintaining the cleanliness of systems is the best method to prevent MIC. Once biofilms have established themselves, it is difficult to get rid of the bacteria entirely. There is a need to implement a better means of destroying biofilms and also to develop environmentally friendly biocides. It is virtually impossible for designers/maintainers to stay abreast of all the technologies and methods used in corrosion prevention and control, so outside professional assistance is usually required. To optimize MIC prevention and control, subject matter experts should be consulted when designing new systems where MIC has traditionally been prominent, for setting up preventive maintenance procedures for new systems, and for other related problems as they arise. Ideally, all problems should be thoroughly documented and entered in an information system for effective use in designing future systems.

NOTES & REFERENCES

Picture on Article Title Page: NASA Astrobiology Academy, Ames Research Center, (http://academy.arc.nasa.gov/2003/ mirpics.htm)

* Hydrotesting is used to check system integrity subsequent to manufacture. A system is filled with water and pressurized to check for leaks, especially around weldments.

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Material Failure Modes, Part I

Material

A Brief Tutorial on Fracture, Ductile Failure, Elastic Deformation, Creep, and Fatigue

This issue of MaterialEASE is Part One of a three part series on material failure modes. It introduces the concept of material failure and covers a number of failure modes, including brittle and ductile failure, elastic distortion, creep, and fatigue. Future MaterialEASE articles will cover other important failure modes including impact, wear, thermal shock and corrosion. This series will make a valuable desk reference for any professional making material selection and design decisions. - Editor

What do design engineers and failure analysis experts have in common? Answer: material failure. These two groups are the bookends to a material's life. While materials selection is sometimes left up to a bona fide materials engineer, designers are typically responsible for determining what environments and operating conditions a component will encounter during service. In many cases designers are also responsible for performing the task of materials selection. This combined role essentially determines the fate of a material and quite possibly the system. Failure analysis specialists explore the questions of how and why a particular system, and more precisely, a material failed. To preclude failure the designer should consider the questions of when and how the system, and more specifically, the material will fail. The first step toward preventing failure is understanding how it might occur.

If a material were resistant to all failure modes in all environments, a system or component could theoretically have an infinitely long life. Unfortunately, all materials are susceptible to failure. Even the best engineered materials are prone to failure given a sufficiently harsh service environment, or if they are poor choices for a specific application. Furthermore, there are a number of mechanisms and combinations of mechanisms that cause materials to fail. The goal of the design engineer is to cost-effectively design a system that operates at its maximum efficiency for the longest possible period of time without having to be replaced or overhauled. To meet this goal it is important for the designer to be aware and have a certain level of understanding about how materials can fail.

The intent of this article is to provide an educational reference for designers and other engineers on the common modes of material failure. Understanding potential failure modes in the early stages of system design can lead to a more appropriate selection of materials, prevent premature system failure and possibly lengthen system life; ultimately resulting in increased safety in some cases and reduced cost of ownership.

INTRODUCTION TO FAILURE

The failure of a material is not restricted to fracture or total disintegration; it can also consist of a change in shape, loss of material or the alteration of mechanical properties. When a material becomes unable to execute the function that it was originally intended or designed to perform, it has failed.

Environmental conditions and operating loads are often the primary causes leading to a material's failure. Examples of harsh environments that commonly induce failure include corrosive, high temperature, and high energy environments. Stress, impact, and frictional loading are examples of operating conditions that frequently cause a material failure. Combinations of harsh environments and mechanical loads often lead to a more rapid material wearout and failure.

There are several failure prevention methods that can be employed, but often the first critical step is to properly select the material or material system that will be used to construct the given system component. Further prevention measures (e.g. protective coatings, cold working, etc.) can be implemented depending on the application, the conditions found in the operational environment, mechanical loading, and the failure modes that the selected material is traditionally susceptible to in a given system configuration. The rest of this article is devoted to providing a background on the most common material failure modes.

FAILURE MODES

There are more than twenty different recognizable ways a material can fail, including the most common forms: fracture, fatigue, wear, and corrosion.[1] Each of these and other common failure modes are described briefly in the following sections or will be featured in the next two issues of *MaterialEASE*.

Brittle Fracture

Brittle fracture occurs when mechanical loads exceed a material's ultimate tensile strength causing it to fracture into two or





Figure 1. Brittle Fracture Surface of a High-Strength Chain. Fracture Began in a Small Crack Resulting from a Heat Treating Problem (Photo Courtesy of Sachs, Salvaterra & Associates, Inc.).



Figure 2. Yielding Failure of UH-1 Helicopter Engine Shaft and Bearing Components[2].

more parts without undergoing any significant plastic deformation or strain failure. Material characteristics and defects such as notches, voids, inclusions, cracks, and residual stresses are the typical initiation points for the formation of a crack leading to brittle fracture (Figure 1). Once the crack is initiated the material will undergo catastrophic failure fairly quickly under a sustained load. There is little energy absorbed (compared to ductile fracture) during the brittle fracture process. This failure mode commonly occurs in brittle materials such as ceramics and hard metals.

Eliminating or minimizing surface and internal material defects is an important method in improving a material's resistance to brittle fracture. Many of these defects originate during material fabrication or processing steps. Therefore, it is important to give these early stages in the life cycle proper attention in order to reduce the material's susceptibility to brittle fracture. Fabricating a part with a smooth surface is also important in preventing brittle fracture. For instance, sharp textures and notches on the surface of the material can initiate brittle fracture. Careful handling of the material after it's produced will also help to prevent unnecessary mechanical damage such as scratches and gouges, which can ultimately lead to brittle fracture. Finally, an appropriate materials selection process to choose a suitable material for the intended application is important in ensuring that it will be capable of handling the applied mechanical loads.

Ductile Failure

Ductile materials that are subjected to a tensile or shear stress will elastically or plastically strain to accommodate the load and absorb the energy. Yielding occurs when the material's yield strength is exceeded and can no longer return to its original shape and size. This is followed by ductile fracture which occurs when the deformation processes can no longer sustain the applied load. Both of these failure modes are described in more detail below.



Figure 3. (a) Ductile Fracture of 2 1/2 Inch Hose Fitting (b) Close-up of the Deformed Region Where a Pin Joining the "Ears" Became Free from the One on the Right Causing the Deformation and Fracture of the One on the Left (Photos Courtesy of Sachs, Salvaterra & Associates, Inc.).



Figure 4. (a) Compressive Buckling Failure of Metal Cylinder, (b) Torsional Buckling Failure of an F-18 Engine Shaft[2].

Yielding

Yielding failure (also known as gross plastic deformation) occurs when a material subject to mechanical loading exhibits sufficient plastic deformation such that it can no longer perform its intended function. This mode of failure results in deflected, stretched, or otherwise misshapen components, and is typical in ductile materials such as metals and polymers. Ceramics and very hard metals are inherently brittle materials and therefore yielding is not a significant concern. An example of this type of failure is often observed in ductile materials subjected to a tensile stress. These malleable materials tend to absorb the applied load by undergoing plastic deformation, which causes an elongation of the material. Yield strength is a measurement of a material's resistance to yielding failure, and it denotes the stress at which the material begins to exhibit a disproportionate increase in strain with increasing stress. Figure 2 shows a picture of several misshapen helicopter components that experienced yielding failure.

Ductile Fracture

A failure mode that is somewhat opposite in nature to brittle fracture is ductile fracture. Ductile fracture occurs when a material experiences substantial plastic deformation or strain while being stressed beyond its yield strength and is consequently torn in two pieces. An extensive amount of energy is absorbed during the deformation process. Similar to brittle fracture, however, cracks are typically nucleated at material defects, such as voids and inclusions. As ductile materials experience plastic deformation, existing voids coalesce to form the crack tip. The actual crack propagation process in ductile fracture is generally a slow process with the crack growing at a very moderate rate as voids coalesce at the fracture surface. An obvious but important consideration is that this type of failure is common in ductile materials, typically metals and polymers.

Failures attributed only to ductile fracture are not common, but rather this mechanism is typically a contributing factor in the overall material failure. When a material does fail due to ductile fracture it is most likely because the stress exceeded the material's strength limits. This indicates that the material chosen during design did not meet the performance requirements, the loads applied were more than what was predicted, the material was improperly or poorly fabricated, or defective raw materials were used for component fabrication.[3] Figure 3 shows pictures of a component that failed by ductile fracture.

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The best method for preventing a part from failing due to ductile fracture is to perform proper materials selection during the design stages of a system. In addition, appropriate quality control procedures should be in place for producing the materials in order to reduce the number of defects. An appropriate materials selection process will ensure that the operating loads imposed as stresses on the chosen material will not exceed its mechanical limits. However, design errors such as inaccurately predicting mechanical loads have been known to occur. Underestimating a load for instance, could lead to ductile fracture.

Buckling

Buckling occurs when a material subjected to compressive or torsional stresses can no longer support the load, and it consequently fails by bulging, bending, bowing or forming a kink or other unnatural characteristic. Bars, tubes, and columns are shapes that are commonly susceptible to failure by buckling. In addition, I-beams and other more complex geometries may experience buckling under compressive or torsional loads. Strength and hardness properties do not indicate a material's susceptibility to buckling. Buckling is dependent on the shape and respective dimensions of the material as well as the modulus of elasticity, which is dependent on temperature. Therefore, buckling is more likely to occur at higher temperatures where the modulus of elasticity is lower, since materials have a tendency to soften when they are heated. Figure 4 (a) shows a picture of a cylindrical metal component after buckling under compressive stress, and (b) a picture of a cylindrical aircraft component that failed by torsional buckling.

Elastic Distortion

A material can fail without being permanently changed when it is elastically deformed to such an extent that it fails to perform its intended function. Elastic deformation occurs when a material is subjected to a load that does not exceed its yield strength. This non-permanent distortion can cause the material, for example, to obstruct another component in a system resulting in failure. Elastic distortion can be induced by a load and affected by a change in temperature. For example, a material's elastic modulus is temperature dependent, and if an unanticipated temperature change occurs the material may undergo elastic deformation at a smaller load than it would at the normal operating temperature. Selection of a material with a sufficiently high modulus to withstand loads without experiencing elastic deformation can prevent this type of failure from occurring,

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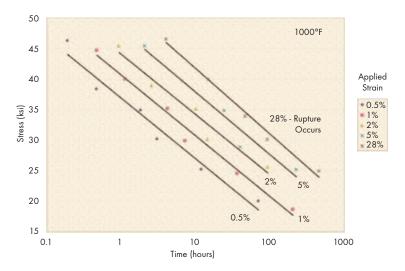


Figure 5. Creep and Rupture Data for 4130 Steel at 1000°F[4].

especially if there is an unanticipated temperature change. Control over operating conditions so that the material does not observe load or temperature changes that would compromise its ability to withstand elastic deformation will also help prevent this type of failure from occurring.

Creep

Creep is a time-dependent process where a material under an applied stress exhibits a dimensional change. The process is also temperature-dependent since the creep or dimensional change that occurs under an applied stress increases considerably as temperature increases. A material experiences creep failure when the dimensional change renders the material useless in performing its intended function. Sufficient strain or creep can result in fracture, known as stress rupture, which is discussed briefly in a subsequent section. Figure 5 shows the time-dependent nature of creep failure.

Creep occurs when vacancies in the material's microstructure migrate toward grain boundaries that are oriented normal to the direction of the applied stress. As this happens atomic diffusion occurs in the opposite direction to fill the voids, resulting in an elongation of the grain in the direction parallel to the applied stress. Other mechanisms of creep include those where vacancies migrate along grain boundaries, dislocations move to accommodate the applied stress in the form of strain, and adjacent grains slide along their common grain boundary also to accommodate the applied stress.[5]

Materials experience thermally activated creep at different temperatures. For example, some materials, such as nickel-based superalloys, are susceptible to creep at relatively high temperatures (e.g. 1000 - 1200°C), while others, such as polymers or tin-lead solder, can be susceptible to creep at much lower temperatures (e.g. 25°C). Generally, creep should be a consideration when a material is operating at a temperature that is greater than $0.3T_m$, where T_m is the material's absolute melting temperature. At $0.5T_m$ creep is very much a concern.[5]

Creep can occur in ceramics at temperatures above 0.4 to $0.5T_{\rm m}$, although it is much more common in metals and polymers. [6] Ceramics have a very high resistance to deformation by creep partly because of their characteristically high melting temperatures. However, at extremely high temperatures ceramics can exhibit a considerable amount of creep.

To prevent failure due to creep deformation it is very important to know the operating conditions of the system when selecting materials for an application. Creep has been a particular problem for turbine engine blades since they experience a sustained stress over time at a relatively high temperature. As a result, materials with high melting temperatures are often selected for such an application. Furthermore, it is important to ensure quality material fabrication and processing in order to reduce material defects and voids.

Creep Buckling

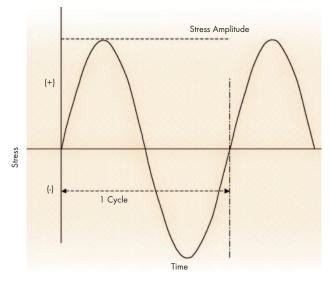
Creep buckling is a failure mode that occurs when the creep process renders a material unable to support loads it could otherwise handle, and as a result the material buckles.

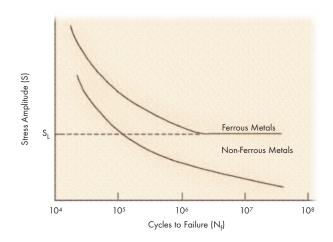
Stress Rupture

Stress rupture, also known as creep fracture, is a mechanism that is closely related to creep except that the material eventually fractures under the applied load. As discussed in the previous section, creep is the time- and temperature-dependent elongation of a material that is subjected to a stress. When this stress overcomes the material's ability to strain, it will rupture. Cracking that precedes the rupture of the material can be either transgranular or intergranular*.

Thermal Relaxation

Thermal relaxation is a process related to the temperaturedependent creep failure mode. Failure by thermal relaxation commonly occurs in fastener materials or other materials that are prestressed such that they could support a greater load than their non-prestressed counterpart. As the material undergoes creep at high temperatures their residual stresses are relieved which may render the material unable to support the given load.





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Figure 7. S/N Curves for Ferrous and Non-Ferrous Metals[8].

Figure 6. Fatigue Loading Cycle.

Fatigue

Fatigue is an extremely common failure mode and deserves considerable attention because it can inflict damage on a material at a stress level that is far less than the material's design limit. Fatigue has been attributed with playing a role in approximately 90% of all material structural failures.[6]

A material that fractures into two or more pieces after being subjected to a cyclic stress (fluctuating load) over a period of time is considered to have failed by fatigue. The maximum value of the cyclic stress (stress amplitude) for fatigue failure is less than the material's ultimate tensile strength. It is often the case that the maximum value of the cyclic stress is so low that if it were applied at a constant level the material would be able to easily support the load without incurring any damage. Cyclic loads cause the initiation and growth of a crack, and ultimately, when the crack is significant enough such that the material can no longer support the load, the material fractures.

The fatigue failure mechanism involves three stages: crack initiation, crack propagation, and material rupture. Similar to both ductile and brittle fracture, fatigue cracks are often initiated by material inhomogeneities, such as notches, grooves, surface discontinuities, flaws, and other material defects.[7] These inhomogeneities or initiation points act as stress raisers where the applied stress concentrates until it exceeds the local strength of the material and produces a crack. The best way to prevent fatigue failure is to keep fatigue cracks from initiating, which can be accomplished by removing or minimizing crack initiators, or by minimizing the stress amplitude. Once fatigue cracks have been initiated they will seek out the easiest or weakest path to propagate through the material. Therefore, minimizing the number of internal material defects, such as voids and inclusions, will increase the time it takes a crack to propagate. Finally, when the crack has weakened the material to a point such that it can no longer support the applied load it will rupture, which can occur by shear or by tension.[7]

Fatigue is not so much dependent on time as it is the number of cycles. A cycle consists of an applied stress being increased from a starting value (in some cases, zero or even negative) up to a maximum positive value (material loaded in positive direction) and then decreasing past the starting point down to a minimum value (in some cases this is a maximum negative loading), and finally back up to the starting value. This cycle is illustrated in Figure 6, where there is positive and negative loading. However, negative loading is not required for fatigue to occur; rather, it can be a fluctuating positive load. Moreover, the stress cycles do not need to be symmetric, but can be randomly changing. In general, ferrous, or iron alloy, materials do have a *fatigue* (*endurance*) *limit* (S_L), which is the stress level (amplitude) under which no failure will occur regardless of the number of



Figure 8. Torsional Low-Cycle Fatigue Fracture of a Shaft. (Photo Courtesy of Sachs, Salvaterra & Associates, Inc.)



cycles. On the other hand, by increasing the stress amplitude, the fatigue failure will commence after a smaller number of cycles. Non-ferrous alloys, such as aluminum and titanium, do not have a fatigue limit. This concept is demonstrated in Figure 7.

Metals and polymers are typically susceptible to fatigue failure, while ceramics tend to be resistant. There are several different types of fatigue including high-cycle fatigue, low-cycle fatigue, thermal fatigue, surface fatigue, impact fatigue, corrosion fatigue, and fretting fatigue. Each of these will be discussed in some detail in the following sections.

High-Cycle Fatigue

High-cycle fatigue is defined as fatigue where the material is subjected to a relatively large number of cycles before failure occurs. Generally, for the fatigue mechanism to be considered high-cycle fatigue the number of cycles required to produce failure is greater than 10,000. The deformation exhibited by a material subjected to high-cycle fatigue is typically elastic.

Low-Cycle Fatigue

A fatigue failure that occurs after a relatively small number of cycles is considered to be low-cycle fatigue. Typically, when a material fails due to fatigue after less than 10,000 cycles, it is considered to be low-cycle fatigue. The mechanisms of crack

growth for materials experiencing low-cycle fatigue are similar to the crack growth of a material subjected to a constant stress. The deformation exhibited by a material subjected to low-cycle fatigue is typically plastic (Figure 8). Since the plastic strains in low-cycle fatigue are usually greater than in high-cycle fatigue, the surface defects of the material are not as important as the bulk material properties.[9]

Thermal Fatigue

Simple temperature fluctuations or repeated heating and cooling can impose stresses on a material leading to fatigue damage and potentially failure. Materials generally exhibit a dimensional change or strain to some extent in response to temperature changes. This response can be significant in some materials, especially metals, and can induce thermal stresses on the material if it is mechanically confined in some way. When a material is exposed to conditions of fluctuating temperatures it can cause cyclic fatigue loading, which can result in crack growth and possibly fracture. This process is referred to as thermal fatigue.

Mechanical loading is not required for thermal fatigue to occur, and this failure mode is different from fatigue under fluctuating stress at high temperature. If there is a temperature gradient within the material that is exposed to fluctuating temperatures, it may experience thermal fatigue since different

Table 1. Methods for Reducing or Eliminating Fretting Fatigue[10].

Principle of Abatement or Mitigation	Practical Method
Reduction in surface shear forces	Reduction in surface normal forces
	 Reduction in coefficient of friction with coating or lubricant
Reduction/elimination of stress concentrations	• Large radii
	 Material removal (grooving)
	Compliant spacers
Introduction of surface compressive stress	Shot or bead blasting
	Interference fit
	Nitriding/heat treatment
Elimination of relative motion	 Increase in surface normal load
	Increase in coefficient of friction
Separation of surfaces	Rigid spacers
	Coatings
	Compliant spacers
Elimination of fretting condition	Drive oscillatory bearing
	 Remove material from fretting contact (pin joints)
	Separation of surfaces (compliant spacers)
Improved wear resistance	Surface hardening
	Ion implantation
	Soft coatings
	 Slippery coatings
Reduction of corrosion	Anaerobic sealants
	Soft or anodic coatings

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sections of the material's microstructure will respond unequally to the temperature changes. Failure from thermal fatigue can occur not only from fracture but also from a permanent change in shape.

Thermal fatigue is a significant concern in certain applications such as internal combustion engines, heat exchangers, and turbine engine blades. Metals are especially susceptible to thermal fatigue because they often have a microstructure that is temperature dependent. Composites are susceptible to thermal fatigue because they consist of multiple unique materials which respond differently to temperature changes. For example, upon temperature fluctuations the reinforcing material can exhibit significant strain while the matrix material experiences minimal strain. This leads to a fatigue type loading on the matrix material, which can result in the initiation of a crack. The best way to mitigate thermal fatigue in composite materials is to choose a reinforcement material and a matrix material that have similar thermal expansion coefficients.[5]

Surface Fatigue

The *MaterialEASE* in the next issue of the *AMPTIAC Quarterly* will contain a brief description of this failure mode.

Impact Fatigue

Impact fatigue occurs when a material is subjected to repeated impacts to a localized area causing the initiation and propagation of a fatigue crack. This repeated impact loading can ultimately result in fatigue fracture.

Corrosion Fatigue

For an in-depth discussion on corrosion fatigue and how it differs from stress corrosion cracking read the article in this issue of the *AMPTIAC Quarterly* entitled: *Environmentally-Assisted Cracking*.

Fretting Fatigue

Fretting damage⁺ on the surface of a material can act as a nucleating point for a crack. Under cyclic loading (typically small amplitude loading) the nucleation of a crack at the location of fretting damage and the subsequent crack propagation and fracture of the material constitutes fretting fatigue. Fretting of a component under fatigue conditions will lead to a much quicker nucleation of cracks than fatigue of a component not subjected to fretting. Furthermore, cracks can be initiated by fretting damage at a much lower stress than if the material is in a normal, undamaged condition. The fatigue strength[‡] of a material can be reduced by up to 70% under fretting conditions.[10] Fretting fatigue is a particularly problematic failure mechanism because it can occur in hidden areas and result in the sudden, catastrophic failure of a component. Joints, bearings, axles and shafts are typically very susceptible to fretting fatigue. [10, 11] Methods for reducing damage by fretting fatigue are briefly described in Table 1.

Creep-Fatigue Interaction

At elevated temperatures creep and fatigue can act simultaneously to produce a concerted, harmful effect on a material. A material operating in high temperature conditions can experience both creep strains and cyclic strains that can seriously compromise the material's expected lifetime. For example, if a material experiences creep strains while undergoing fatigue cycling, its fatigue life can be greatly reduced. Similarly, if a material experiences fatigue cycling while undergoing creep, its creep life can be significantly reduced. The combined effect of creep and fatigue can pose serious problems for those designing a system to perform for a defined lifetime. There has been significant research into predicting the combined effects of creep and fatigue on materials in various operating conditions.[12]

FAILURE PREVENTION

In general, the most effective ways to prevent a material from failing is proper and accurate design, routine and appropriate maintenance, and frequent inspection of the material for defects and abnormalities. Each of these general methods will be described in further detail below.

Proper design of a system should include a thorough materials selection process in order to eliminate materials that could potentially be incompatible with the operating environment and to select the material that is most appropriate for the operating and peak conditions of the system. If a material is selected based only on its ability to meet mechanical property requirements, for instance, it may fail due to incompatibility with the operating environment. Therefore, all performance requirements, operating conditions, and potential failure modes must be considered when selecting an appropriate material for the system.

Routine maintenance will lessen the possibility of a material failure due to extreme operating environments. For example, a material that is susceptible to corrosion in a marine environment could be sustained longer if the salt is periodically washed off. It is generally a good idea to develop a maintenance plan before the system is in service.

Finally, routine inspections can sometimes help identify if a material is at the beginning stages of failure. If inspections are performed in a routine fashion then it is more likely to prevent a component from failing while the system is in-service.

CONCLUSION

From a research standpoint, engineers must consider all plausible material failure modes when developing and maturing a new material or when 'evolving' an old material. However, material failure can often be the result of inadequate material selection by the design engineer or their incomplete understanding of the consequences for placing specific types of materials in certain environments. Education and understanding of the nature of materials and how they fail are essential to preventing it from occurring. Simple fracture or breaking into two pieces is not all-inclusive in terms of



failure, because materials also fail by being stretched, dented or worn away. If potential failure modes are understood, then critical systems can be designed with redundancy or with fail-safe features to prevent a catastrophic failure. Furthermore, if appropriate effort is given to understanding the environment and operating loads, keeping in mind potential failure modes, then a system can be designed to be better suited to resist failure.

MaterialEASE 30 will be published in *AMPTIAC Quarterly*, Volume 9, Number 2, and will contain the next installment of failure modes. These will include: Impact, Spalling, Wear, Brinelling, Thermal Shock, and Radiation Damage.

ACKNOWLEDGEMENT

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NOTES & REFERENCES

* Transgranular indicates that a crack proceeds through grain boundaries and across the grain, whereas, intergranular indicates that a crack navigates around or between grain boundaries. † Fretting wear is a damage mechanism whereby two surfaces that are in intimate contact with each other and subjected to a small amplitude relative motion (cyclic in nature) tend to incur wear. The *MaterialEASE* in the next issue of the *AMPTIAC Quarterly* will contain a brief description of this failure mode.

 \ddagger Fatigue strength is the maximum stress that a material can endure without failure for a given number of cycles.

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... Don't forget to look for Material Failure Modes Parts 2 & 3 in upcoming issues of MaterialEASE!

Materia

The AMPTIAC Quarterly, Volume 9, Number 1

16

Environmentally-Assisted Cracking:

Comparing the Influence of Hydrogen, Stress, and Corrosion on Cracking Mechanisms

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INTRODUCTION

Cracking is possibly the most common material failure mode, and may be the most dangerous, as complete fracture can occur nearly instantaneously and without any advance warning. Harsh environments can compound the cracking problem as they often supplement the mechanisms that are tearing the material apart, thereby accelerating the rate of failure. Environmentallyassisted cracking is a very broad and complex subject area in terms of the various mechanisms through which it can occur. It can generally be classified into three different forms: stress corrosion cracking (SCC), corrosion fatigue (CF) and hydrogenassisted cracking (HAC). It is important to distinguish between these three forms, as they can appear to be very similar in nature despite some fundamental differences.

Each type of environmentally-assisted cracking is described in the following sections, along with their typical mechanisms, influencing factors, and mitigation and prevention strategies. The last section provides a comparison of some of the key differences and similarities between the three phenomena. Hydrogen-assisted cracking is described first since it commonly plays a role in both SCC and CF.

HYDROGEN-ASSISTED CRACKING

The presence of hydrogen has the ability to influence the mechanical integrity of a metal, thus making it more susceptible to cracking. If hydrogen is transported to a localized region, such as a crack tip, it can accelerate the crack growth rate. Hydrogen can be introduced to a metal through a number of media, as it is present in water, air (gaseous hydrogen, water vapor, pollution, etc.), and many other substances.

Hydrogen plays a role in a number of cracking mechanisms, including stress corrosion cracking, corrosion fatigue, and fatigue cracking. However, there are cracking phenomena that occur under constant stress loads and in which hydrogen plays a significant part, but corrosion processes are absent. These are considered separate cracking mechanisms from SCC, CF, and general fatigue. Furthermore, hydrogen can induce minor damage to a material, which may not result in the fracture of that material.

The phrase *hydrogen-assisted cracking* has been loosely defined and encompasses a number of different mechanisms, and in some cases is considered to be interchangeable with the phrases *hydrogen-induced cracking, hydrogen embrittlement,* and *hydrogen damage.* For the purpose of this article, HAC is considered to be anything where hydrogen plays a major role in the initiation or propagation of cracks. Some of the mechanisms where hydrogen contributes to the failure of a material by stress corrosion cracking or corrosion fatigue will be discussed in their respective sections.

Cracks that have been propagated with the assistance of hydrogen typically are not significantly branched and can be either intergranular or transgranular. Materials that experience HAC usually do not exhibit much plastic deformation, thus the fracture that occurs in response to HAC mechanisms typically is brittle fracture. The multiple hydrogen damage mechanisms can act together or alone to initiate and propagate cracks. Mechanisms of HAC are described in the following section.

Hydrogen-Assisted Cracking Mechanisms

One mechanism of HAC involves the diffusion and buildup of gaseous hydrogen (H_2) in a void region of the metal (e.g. crack space, microstructural void). This process can easily occur if the structure is exposed to a hydrogen-rich environment. This gaseous hydrogen exerts a pressure against the walls of the metal, thus assisting in propagating the crack, or initiating a crack in the case where one doesn't already exist (i.e. when gas collects in a void). The latter process can occur when H₂ gas is "pushing" against the metal from the inside and augments the stress load being applied to the material so that the total stress exceeds that required to initiate a crack. This effectively creates an area of stress concentration and a nucleating site for a crack. The propagation of a crack is also assisted with the pressure of the hydrogen gas pushing against the crack walls from the inside, which again works in combination with the stress applied to the metal.

A second general mechanism of HAC occurs with hydrogen adsorbing to the metal surface, thereby reducing the surface energy of the metal at that point. The reduction of surface energy can then facilitate the initiation of a crack, or can enhance the propagation rate of the crack.

The third general mechanism of HAC involves atomic hydrogen migrating into the microstructure of the metal. This results in a reduction of the interatomic bond strength of the metal, which provides a point of nucleation for a crack or accelerates the crack propagation process.

Forms of Hydrogen Damage

There are a number of different forms of hydrogen damage that apply to metallic materials, resulting from the combined factors Table 1. Metals' Susceptibilities to Hydrogen Damage[1].

Hydrogen- Induced Cracking	Hydrogen Embrittle- ment	Loss in Tensile Ductility	High Temperature Hydrogen Attack	Blistering	Shatter Cracks, Flakes, Fisheyes	Micro- perforation	Degradation in Flow Properties	Metal Hydride Formation
Steels	Carbon and	Steels	Carbon and	Steels	Steels	Steels	Iron	V
Nickel-alloys	low-alloy	Nickel-alloys	low-alloy	Copper	(forgings and	(compres-	Steels	Nb
Metastable	steels	Be-Cu	steels	Aluminum	castings)	sors)	Nickel-alloys	Та
stainless steel		Bronze						Ti
Titanium-		Aluminum-						Zr
alloys		alloys						U

of hydrogen and residual or applied tensile stresses. Hydrogen damage can result in cracking, embrittlement, loss of ductility, blistering and flaking, and also microperforation. These and other types of hydrogen damage are briefly described in the following sections. Table 1 provides lists of general types of metals that are typically susceptible to the various types of hydrogen attack.

Hydrogen-Induced Cracking

Hydrogen-induced cracking 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 ultimately initiating the observed damage.

Hydrogen Embrittlement

Hydrogen embrittlement is the brittle cracking or fracture of a ductile alloy during plastic deformation in a hydrogen gas containing environment.

Loss of Tensile Ductility

The loss of tensile ductility sometimes occurs in metals exposed to hydrogen, resulting in a significant decline in elongation and reduction in area properties. It is most often observed in low strength alloys, but has also been observed in some steels, stainless steels, aluminum alloys, nickel alloys, and titanium alloys.

High Temperature Hydrogen Attack

High pressure hydrogen will attack carbon and low-alloy steels at high temperatures. This occurs when hydrogen diffuses into the metal and reacts with carbon, resulting in the formation of methane. This in turn results in decarburization of the alloy and possibly the formation of cracks.

Blistering

Blistering occurs primarily in low strength metals. It is a result of atomic hydrogen diffusion into defect areas of the alloy. The monotonic atoms combine into gas molecules in voids within the metal. Then, the high pressure of H_2 entrapped within the metal causes the material to blister or rupture. This form of attack has been observed in low strength steels exposed to hydrogen sulfide (H_2S) or when cleaned in pickling baths.

Shatter Cracks, Flaking, and Fish Eyes

These forms of hydrogen damage are similar to blistering and are seen primarily during processing. Hydrogen is more soluble at the melting temperatures of metals allowing it to enter defect areas. The decreased solubility of hydrogen when cooled then produces the damage features.

Microperforation

Microperforation has been observed in steels in a high pressure hydrogen and room temperature environment. The hydrogen produces fissures in steel alloys, such that gases and liquids can permeate the material.

Degradation in Flow Properties

An increase in creep rate can occur in iron alloys and steels under ambient conditions in hydrogen environments, and in several other alloys at elevated temperatures.

Hydride Formation

The precipitation of metal hydride phases in magnesium, tantalum, niobium, vanadium, uranium, zirconium, titanium, and their alloys, in the presence of hydrogen results in a degradation of mechanical properties and cracking.

Managing Hydrogen Damage

Methods to protect against or mitigate hydrogen damage include:

- Limit hydrogen introduced into the metal during processing.
- Limit hydrogen in the operating environment.
- Structural designs to reduce stresses (below threshold for subcritical crack growth in a given environment).
- Use barrier coatings.
- Use low hydrogen welding rods.
- Select appropriate materials resistant to hydrogen damage.

STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) is an environmentally-induced phenomenon that occurs when a metal is subjected simultaneously to a tensile stress and a corrosive environment. 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 the cause of cracking that occurs when the surface of a metal is corroded, resulting, in the creation of a nucleating point for a crack. Rather, it is a synergistic effect of a corrosive agent and a modest, static tensile stress. If either the corrosive media or the tensile stress were absent, the effect would not be the same, and might be absent completely. Another form of corrosion similar to SCC (although with a subtle difference) is corrosion fatigue, which is discussed in the next section. The key difference is that SCC occurs with a static stress, while corrosion fatigue requires a cyclic stress. Figure 1 shows a micrograph of a cadmium-plated steel with SCC damage.

SCC is a process that takes place within the material, where the cracks propagate through the internal structure, usually leaving the outer surface unharmed. Furthermore, there are two main types of SCC: intergranular and transgranular. For the intergranular form, the cracking progresses mostly along grain boundaries, whereas in transgranular SCC, the cracking does not strictly adhere to the grain boundaries, instead it can penetrate grains. Figure 2 illustrates the two types of stress corrosion cracking. Stress corrosion crack propagation typically occurs in a stable or steady-state fashion. However, as will be discussed in the section on SCC mecha-

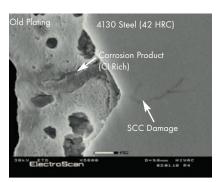


Figure 1. Cadmium Plated Steel Rocket Motor with SCC Damage[2].

nisms, the crack propagation process can be discontinuous. Most cracks tend to propagate in a direction that is perpendicular to the direction of applied stress. Aside from an applied 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, but the crack initiation mechanisms are often complicated. Other initiation sites include fabrication defects, imperfections as a result of machining (e.g. end grains), and material flaws.

SCC is a concern in alloys that produce a surface film in certain environments, such as an oxide film on aluminum, since the film may protect the alloy from other forms of corrosion, but not SCC. Moreover, SCC is a dangerous form of corrosion because it can be difficult to detect, and it can occur at stress levels well within the range that the metal is designed to handle. The stress corrosion cracking stress intensity factor, K_{scc} , is typically much less than the critical stress intensity factor, K_{crit} .[4] This indicates that cracking can occur at much lower stress intensity values with the simultaneous action of corrosion than it can under conditions where corrosion is absent. Additionally, the mechanism of SCC is not completely understood. There are a number of proposed mechanisms that attempt to explain the phenomenon, but there is not one that can describe each instance of SCC.

Stress Corrosion Cracking Mechanisms

There is no mechanism that completely describes all cases of stress corrosion cracking, but there have been a number of proposed mechanisms for the phenomenon, which can be classified either as an anodic SCC mechanism or a mechanical fracture process. These mechanisms (described below) can act alone or in conjunction with one another to produce SCC.

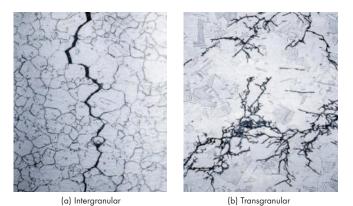


Figure 2. Pictures of Stress Corrosion Cracking. [3] (Courtesy of Metallurgical Technologies, Inc.)

Anodic SCC involves the rupture of the protective oxide layer (formed from corrosion of the base metal) at the crack tip, anodic dissolution of the base metal, and crack growth under constant stress. Crack growth can be either intergranular or transgranular (shown in Figure 2).[5] There are a number of SCC mechanisms classified under the mechanical fracture process group. Descriptions of several of these follow.

Corrosion of the base metal can cause tunnels to form, originating from the crack tip. These tunnels degrade the strength of the metal, and when the stress intensity becomes too great, the crack propagates further. Then the process starts over again, with corrosion causing the formation of more tunnels at the same crack tip.[5]

Another mechanism involves exposure to aggressive species from the surrounding environment, which can chemically adsorb (form a chemical bond with the base metal) to the surface of the crack tip and aid in the propagation of the crack. The adsorption of these species assist in the formation of dislocations near the crack tip. These dislocations and the constant stress applied to the metal cause plastic deformation of the metal near the crack tip, resulting in further propagation of the crack.[5]

A similar mechanism has been suggested where a species from the surrounding environment adsorbs to the surface of the metal, reducing the bond strength between adjacent atoms in the metal lattice structure. This results in an overall decrease in material strength in which the stress required to cause brittle fracture is reduced. This crack propagation mechanism is continuous and is controlled by the rate of mass diffusion of the environmental species to the crack tip.[5]

A mechanism for discontinuous stress corrosion crack propagation involves the cyclic formation and rupture of a protective film at the crack tip on a base metal. When a metal is exposed to a corrosive environment, it will often form a protective film at the surface. With an applied stress, the film, which is typically brittle, can rupture and consequently expose the surface of the base metal and crack tip to the corrosive environment resulting in further dissolution. This corrosion of the crack tip aids in the propagation of the crack. The surface of the exposed metal in collaboration with the corrosive environment eventually repairs the protective film, and the process starts over again.[5]

A similar concept has been proposed where a film forms at the surface of a metal, and brittle fracture is induced by dealloying and/or vacancy injection. The crack proceeds through the film
 Table 2. Materials, Environmental and Mechanical Factors that

 Influence Stress Corrosion Cracking.

Materials Factors	Environmental Factors	Mechanical Factors
Composition	Temperature	Stress
Microstructure	рН	Strain rate
Contaminants	Electrochemical	
or impurities	Potential	
Grain size	Solute species	
Grain orientation	Solute concentration	
	Oxygen concentration	

and across the film/metal interface into the metal where it propagates under the stress of the applied load. Once the crack stops, the process starts over with the formation of the film.[5]

The last mechanism worth mentioning is a combination of hydrogen-assisted cracking (described earlier in this article) and SCC. Corrosion reactions often result in the formation of hydrogen gas. Hydrogen atoms (especially if the partial pressure of the hydrogen is high) can diffuse or are absorbed into the lattice of the metal causing a deterioration of the metal's properties. This, combined with the applied stress to the metal, can result in crack propagation.[5]

Factors Affecting Stress Corrosion Cracking

There are a number of factors that contribute to the occurrence and rate of SCC in metals. Increasing the temperature of a system, for example, often accelerates the rate of SCC. The presence of chlorides or oxygen in the environment can also significantly influence the occurrence and rate of SCC. These factors can be categorized as materials, environmental, or mechanical factors, some of which are listed in Table 2.

From Table 2 it is clear that stress corrosion cracking is dependent on a number of factors. However, certain types of alloys are more susceptible to SCC in particular environments, while other alloys are more resistant to that same environment. Some specific environments that can cause SCC of certain metals are listed in Table 3.

Managing Stress Corrosion Cracking

The composition of a metal has a significant affect on the metal's susceptibility to SCC. Therefore, material selection is very important in preventing SCC from occuring in a system. There are a few maintenance steps that can hinder further growth of pre-existing damage within a material. Depending on the geometry of the component, it may be feasible to use corrosion preventive compounds or to reapply coatings in order to protect the material from further corrosion and slow the crack growth. There are several other methods that may be used to minimize the risk of SCC. Some of these methods include:

- 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).
- Control or modify the environment (e.g. pH, oxygen content, etc.).
- Use surface treatments (shot peening, laser peening) which increase the surface resistance to SCC.
- Barrier coatings will deter SCC as long as they remain intact.

Table 3. Environments that May Cause Stress Corrosion Cracking of Metals[6].

Cracking of Metals[6].				
Material	Environment			
Aluminum alloys	NaCl-H ₂ O ₂ solutions			
	NaCl solutions			
	Seawater			
	Air, water vapor			
Copper alloys	Ammonia vapors and solutions			
	Amines			
	Water, water vapor			
Gold alloys	FeCl ₃ solutions			
	Acetic acid-salt solutions			
Inconel	Caustic soda solutions			
Lead	Lead acetate solutions			
Magnesium alloys	NaCl-K ₂ CrO ₄ solutions			
	Rural and coastal atmospheres			
	Seawater			
	Distilled water			
Monel	Fused caustic soda			
	Hydrofluoric acid			
N 10 1 1	Hydrofluorosilicic acid			
Nickel	Fused caustic soda			
Ordinary steels	NaOH solutions			
	NaOH-Na ₂ SiO ₂ solutions			
	Calcium, ammonium, and sodium nitrate solutions			
	Mixed acids (H ₂ SO ₄ -HNO ₃) HCN solutions			
	Acidic H_2S solutions			
	Seawater			
	Molten Na-Pb alloys			
Stainless steels	Acid chloride solutions (e.g. MgCl ₂ and BaCl ₂)			
	NaCl- H_2O_2 solutions			
	Seawater			
	H ₂ S			
	NaOH-H ₂ S solutions			
	Condensing steam from chloride waters			
Titanium alloys	Red fuming nitric acid, seawater,			
	N_2O_4 , methanol-HCl			
	2 4'			

• Reduce exposure of end grains, which can result from design and/or manufacturing (i.e. end grains can act as initiation sites for cracking because of preferential corrosion and/or a local stress concentration).

CORROSION FATIGUE

Corrosion fatigue (CF) 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). It is often considered to be a component 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. To provide protection against this phenomenon or to design around it, it is important to first understand what corrosion fatigue is and what the mechanisms are that govern it.

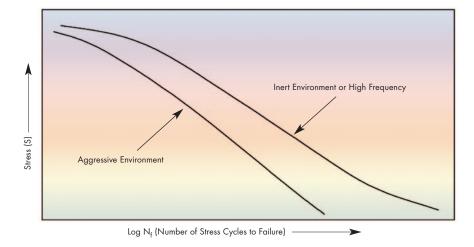


Figure 3. Comparison of Fatigue (S/N) Curves for a Material in an Inert Environment and an Aggressive Environment[7].

Corrosion fatigue is essentially a decrease in fatigue strength due to the effects of electrochemical degradation (corrosive environment), as illustrated in Figure 3. 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. Fatigue cracking is often characterized by "beach marks" or striation patterns which are perpendicular to the crack propagation direction, as shown in Figure 4.

Corrosion Fatigue Mechanisms

Corrosion fatigue is a complex process that no one mechanism can describe completely for all cases. The general mechanism of corrosion fatigue has been described as being hydrogeninduced, the result of anodic dissolution, or a combination of the two. Corrosion fatigue cracks are often initiated at the surface. Subsurface cracks initiate at areas of stress concentration, such as material defects near the surface. Corrosion fatigue

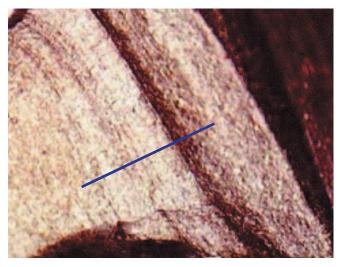


Figure 4. Characteristic Fatigue Striation Pattern (Note the Crack Proceeds Perpendicular to the Striation Marks as Indicated by the Blue Line)[8].

cracks are typically transgranular with little branching. The final failure event of the material is simply a mechanical process without any assistance from corrosion. Thus, at that final stage the mechanism becomes exactly the same as fatigue.

Anodic Dissolution

Anodic dissolution is a very active mechanism for assisting with fatigue cracking in metals, and typically occurs in aqueous environments or environments containing liquids. The mechanism basically consists of three steps. In the first step, the protective oxide film, which is generated through the corrosion reaction between the corrosive environment and the base metal, is ruptured near the crack tip by the fatigue process. The exposed base metal is then attacked by the corrosive media causing dissolution, and consequently sharpening or dulling of the crack tip, depending on the rate of repassivation (the reformation of protective film). During the anodic dissolution, the passive film is repaired, and the corrosion process is stopped. The process then begins all over again with the rupture of the protective film by the fatigue process, thereby exposing the base metal to the corrosive media. This process and the crack growth rate are dependent on the rate of anodic dissolution, rate of repassivation, etc.[9] For example, if the rate of dissolution is much faster than the rate of repassivation, then the crack tip would be blunted.[9]

An effective method for hindering the anodic dissolution mechanism responsible for corrosion fatigue crack propagation is cathodic protection. Cathodic protection increases the rate at which the protective film reforms, thereby reducing the time available for corrosion of the crack tip following rupture of the passive film.[9]

Hydrogen-Induced Mechanisms

The presence of hydrogen at the crack tip can cause damage to the metal and can aid in the propagation of the crack under cyclic loading. Thus, the crack growth rate is accelerated by hydrogen damage. Within the mechanism of hydrogeninduced corrosion fatigue cracking are several different mechanisms by which this hydrogen damage and cracking can occur.

Gaseous hydrogen environments can aid in crack growth through a pressure process in the void space of a crack or

Table 4. Factors Affecting Corrosion Fatigue[9].

Metallurgical	Environmental	Mechanical	Geometrical
Alloy composition	Type of environments	Fatigue load frequency	Crack size
Microstructure and	(gaseous or liquid)	Fatigue load ratio	Crack geometry
crystal structure	Partial pressure of damaging	Fatigue load waveform	Specimen thickness
Heat treatment	species in aqueous or other liquid environments	Maximum stress-intensity	(plane strain versus
Grain boundary structure	Concentration of damaging	factor and stress-intensity-	plane stress)
Grain shape and size	species in aqueous or	factor range	
Surface texture	other liquid environments Temperature	Load interactions in variable amplitude loading (over/	
Distribution of alloy		under/spectrum load)	
elements and impurities	рН	Residual stress	
Deformation mode	Electrochemical potential		
(slip character, twinning, cleavage)	Viscosity of the environment		
Mechanical properties (strength, toughness, etc.)			

microcrack. The relatively high pressure from diatomic hydrogen gas acting as a localized force in the crack region can supplement the stress on the metal and consequently accelerate the crack growth rate. This is considered corrosion fatigue when cathodic reactions associated with the corrosion of a metal release hydrogen atoms that combine to form gaseous hydrogen (H_2), which results in a pressure buildup in the crack void space.[9]

Atomic hydrogen dissolved in a metal can also lead to an increased fatigue crack growth rate. Hydrogen atoms within a metallic crystalline structure can lower the bond strength between the individual atoms. Moreover, hydrogen atoms generated during the corrosion process can diffuse through a metallic structure under an applied stress, and collect near the point of maximum stress. The consequence of dissolved hydrogen in a metal is that it can reduce the strength of the metal, and if a crack exists, it will propagate with less resistance where there is a concentration of hydrogen atoms.[9]

A similar mechanism has been observed when hydrogen is adsorbed on the surface of the metal near the crack tip. The adsorbed hydrogen lowers the surface energy of the metal, which facilitates crack growth. Similarly, species other than hydrogen can adsorb to the surface of the metal, resulting in a decrease in the surface energy and an accelerated crack growth rate.[9]

Metal hydride formation near a crack tip region may also contribute to fatigue crack propagation. Metal hydrides can precipitate near this region when certain metallic alloying elements (e.g. Ti, Ni, Nb, V and Zr have tendencies to form metal hydrides) are exposed to a hydrogen environment. The resulting hydrides are brittle and reduce the strength of the metal at the crack tip, leading to further propagation of the fatigue crack.[9]

Finally, it has been proposed that dissolved hydrogen enables the movement of dislocations by reducing the stress required for migration. This enhances the plastic flow of the metal, which further enables crack propagation.[9]

Factors Affecting Corrosion Fatigue

There are a number of factors that affect the onset of corrosion fatigue and the growth rate of cracks caused by this mechanism. For example, corrosion, such as pitting, causes stress raisers in the vicinity of the pit, much like notch effects. This can lead to crack initiation at a stress below that for a material in a noncorrosive 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. These and other factors influencing corrosion fatigue are provided in Table 4.

Managing 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. However, increased strength normally reduces fracture toughness and vice versa. One method to enhance fracture toughness while maintaining strength is to reduce the metal's grain size. Additionally, a smooth or highly polished surface is more resistant to crack initiation. High temperatures also contribute to corrosion fatigue, thus maintaining operating temperatures at relatively low levels will help minimize its effects. Components exhibiting long cyclic periods of stress typically do not experience any environmental assistance with cracking. Also similar to SCC, maintenance efforts such as using corrosion preventive compounds or reapplying protective coatings to damaged areas may help inhibit corrosion and slow the crack growth rate.

Methods to deter corrosion fatigue include the following:

- 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.

Figure 5. Branching Characteristics of SCC and CF[10].

- 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.

COMPARISON OF SCC, CF, AND HAC

Corrosion fatigue, stress corrosion cracking and hydrogenassisted cracking are similar phenomena in that they are all

environmentally-assisted cracking mechanisms. However, it is important to recognize their differences for the purpose of employing the appropriate prevention techniques. The difference between stress corrosion cracking and corrosion fatigue is that SCC is a crack propagation process in a corrosive environment under a static or sustained tensile stress, whereas CF is the failure of a material through crack propagation by the combined effects of a corrosive environment and cyclic stress loading. At a very low cycle frequency, CF can appear to be nearly indistinguishable from SCC. A visible difference

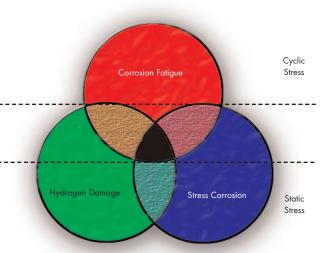


Figure 6. Conceptual Interrelationship of Corrosion Fatigue, Stress Corrosion Cracking and Hydrogen-Assisted Cracking[11].

between SCC and CF is that stress corrosion cracks often have many small branches, while corrosion fatigue cracks have little

assisted cracking. An illustration of the interrelationship between these mechanisms is given in Figure 6. The textured

or no branching. This is illustrated in Figure 5. Critical stress intensity factors for CF are often lower than that for SCC. This

is because CF can more rapidly cause protective oxide films to

rupture, thus exposing the base metal to corrosive conditions,

ultimately resulting in the formation of a crack. Another important difference between SCC and CF is that they are pre-

vented using different methods (although some methods of

prevention are the same, e.g. stress reduction, coatings, surface

Table 5. Characteristics of Environmentally-Assisted Cracking Mechanisms[12].							
Factor	SCC	Corrosion Fatigue	Hydrogen-Assisted Cracking				
Stress	Static tensile	Cyclic + tensile	Static tensile				
Aqueous corrosive agent	Specific to the alloy	Any	Any				
Temperature increase	Accelerates	Accelerates	< Ambient: increases				
Pure metal	Resistant	Susceptible	Susceptible				
Crack morphology	Transgranular, Intergranular, Branched	Transgranular, Unbranched, Blunt tip	Transgranular, Intergranular, Unbranched, Sharp tip				
Corrosion products in cracks	Absent	Present	Absent				
Crack surface appearance	Cleavage-like	Beach marks and/or striations	Cleavage-like				
Cathodic protection	Suppresses	Suppresses	Accelerates				
Near maximum strength	Susceptible but minor	Accelerates	Accelerates				

peening, etc.). Hydrogen-assisted cracking or hydrogen embrittlement can be part of these two mechanisms, but in other cases it can also be characterized as its own mechanism. For example, metals can be damaged in the presence of hydrogen resulting in enhanced stress corrosion or fatigue crack growth rates. Additionally, metals may exhibit cracking that is initiated and/or propagated in the presence of hydrogen without the existence of corrosion mechanisms. This can occur with or without the assistance of a static stress load.

> There are often complex relationships that exist between corrosion fatigue, stress corrosion cracking and hydrogen

areas in the figure represent the combination of two failure mechanisms. The darker area in the center represents the interaction of all three phenomena. The region between the dotted lines indicates a transition from cyclic to static stress or vice versa. For example, extremely low amplitude cyclic stress could be considered to be nearly static. Table 5 provides some of the characteristics of these three environmentally-assisted cracking mechanisms for comparison.

CONCLUSION

There are other environmental conditions such as temperature, radiation, and pH that can have deleterious effects on a material, absent of corrosion and hydrogen, that lead or contribute to crack initiation and/or propagation. However, the most common and often the most severe conditions typically involve a corrosive environment and a static or dynamic load. Materials subject to these conditions can undergo rapid and unanticipated failure because of undetected material defects. Stress corrosion cracking, corrosion fatigue and hydrogen-assisted cracking are often the culprits in these types of failures, which can be catastrophic to certain systems. Understanding and differentiating the three will ultimately lead to more effective strategies in control and prevention, especially through more appropriate material selection.

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* Notch-sensitivity indicates a particular material's susceptibility to fracture that is initiated at a stress raiser, such as a notch, surface defect or scratch. Brittle materials tend to be notch-sensitive. [1] *Environmentally Induced Cracking*, ASM Handbook, Vol. 13: Corrosion, 9th Edition, ASM International, 1987, pp. 145-189

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06/26/05 - 06/30/05 State College, PA Contact: Donna Lucas Materials Research Institute -Penn State University University Park, PA 16802 Phone: 814.865.1656 Fax: 814.865.2326 Email: dzm@psu.edu Web Link: www.mri.psu.edu/conferences

2005 National Space & Missile Materials Symposium

06/27/05 - 07/01/05 Summerlin, NV Contact: M. Kubal; Anteon Corporation 5100 Springfield St, Ste 509 Dayton, OH 45431 Phone: 937.254.7950 ext 1168 Fax: 937.253.2296 Email: mkubal@anteon.com Web Link: www.usasymposium.com

3rd International Conference on Advanced Engineered Wood Composites

07/10/05 - 07/14/05 Bar Harbor, ME Contact: Doreen Parent, The AEWC Center University of Maine, Orono, ME 04469 Phone: 207.581.2123 Email: doreen.parent@umit.maine.edu Web Link: www.aewc.umaine.edu/conference

2005 World Summit on Advanced Capacitors

07/11/05 - 07/13/05 San Diego, CA Contact: Intertech Corporation 19 Northbrook Dr Portland, ME 04105 Phone: 207.781.9800 Fax: 207.781.2150 Web Link: www.intertechusa.com

2005 Advanced Gun Barrel Materials & Manufacturing Symposium

07/12/05 - 07/14/05 St. Michael, MD Contact: Dr. William de Rosset, USMA United States Military Academy West Point, NY 10996 Email: aw2604@usma.edu Web Link: www.dean/usma.edu/ departments/math/ARL-BENET GUNSYMPOSIUM/

Interdisciplinary Transport Phenomena in Microgravity & Space Sciences IV

08/07/05 - 08/12/05 Contact: Engineering Conferences International Six Metro Tech Center Brooklyn, NY 11201 Phone: 718.260.3743 Fax: 718.260.3754 Email: info@eci.poly.edu Web Link: www.engconfitl.org/5aw.html

The Integrated Systems Health Management (ISHM) Conference

08/08/05 - 08/11/05 Cincinnati, OH Contact: Ms. Cathy Griffith; Anteon Corp. 5100 Springfield Pike, Ste 509 Dayton, OH 45431 Phone: 937.254.7950 Email: cgriffith@anteon.com Web Link: www.usasymposium.com/ishm

12th International Conference on Environmental Degradation of Materials in Nuclear Systems-Water Reactors

Systems-water Reactors 08/14/05 - 08/18/05 Salt Lake City, UT Contact: TMS Meeting Services 184 Thorn Hill Rd Warrendale, PA 15086 Phone: 724.776.9000 ext 243 Fax: 724.776.3770 Email: mtgserv@tms.org Web Link: www.tms.org/Meetings

6th Pacific Rim Conference on Ceramic & Glass Technology

09/11/05 - 09/16/05 Maui, HI Contact: Dr. Sylvia M. Johnson, PacRim 6 Program Chair, NASA Ames Research Center; NASA Ames Research Moffet Field, CA Web Link: www.ceramics.org/meetings/

International Conference on Silicon Carbide & Related Materials 2005 (ICSCRM 2005)

09/18/05 - 09/23/05 Pittsburgh, PA Contact: TMS Customer Service 184 Thorn Hill Rd Warrendale, PA 15086 Phone: 724.776.9000 ext 243 Fax: 724.776.3770 Email: mtgserv@tms.org Web Link: www.tms.org/Meetings

MS&T '05 (Materials Science & Technology 2005)

9/25/05 – 9/28/05 Pittsburgh, PA Contact: TMS Meeting Services 184 Thorn Hill Rd Warrendale, PA 15086 Phone: 724.776.9000 ext 243 Fax: 724.776.3770 Email: mtgserv@tms.org Web Link: http://doc.tms.org

IMAPS 38th Annual Symposium on Microelectronics

09/29/05 - 10/01/05 Philadelphia, PA Contact: IMAPS-Intl Microelectronics & Packaging Society 611 2nd St, NE Washington, DC 20002 Phone: 202.548.4001 Fax: 202.548.6115 Email: imaps@imaps.org Web Link: www.imaps.org

International Symposium on Superalloys 718, 625, 706 & Derivatives

10/02/05 – 10/05/05 Pittsburgh, PA Contact: TMS Meetings Services 184 Thorn Hill Rd Warrendale, PA 15086 Phone: 724.776.9000 Fax: 724.776.3770 Email: mtgserv@tms.org Web Link: http://doc.tms.org

Army Research Laboratory Celebrates Recent Special Edition of the AMPTIAC Quarterly.

In recognition of the success of the Special Army Materials Issue of the AMPTIAC Quarterly (Volume 8, Number 4), many of its authors assembled recently for a celebration at the Army Research Laboratory's (ARL) offices at Aberdeen Proving Ground, Maryland. Brief welcoming and congratulatory addresses were given by Dr. James McCauley, ARL Fellow, article author, and key coordinator for the issue; and Dr. Steven McKnight, newly-appointed Materials Division Chief, Weapons and Materials Research Directorate (WMRD), and also a contributing author. Also in attendance were other members of the ARL staff, Mr. David Rose (AMPTIAC Director), and Mr. Chris Grethlein (Editor of the AMPTIAC Quarterly).



The highlight of the event was the presentation of the cake, which bore a remarkably sharp image of the issue's cover! The contributors in attendance assembled for a group picture with the cake (in foreground).



Pictured from left to right: William Nothwang, Ernest Chin, Jerry LaSalvia, Pauline Smith, Laszlo Keckskes, Sandra Young, Robert Dowding, Kes Chesonis, John LaScala, Joseph South, James Sands, William Drysdale, Steven McKnight, Robert Carter, Larry Burton (front), Chris Grethlein (AMPTIAC, back), Robert Woodman, James McCauley, David Rose (AMPTIAC).

A Correction... We at the AMPTIAC Quarterly wish to extend our sincerest thanks to our readership – both in print and on-line – for all of the positive reviews and feedback we have received in response to our recent special edition (Volume 8, Number 4), which highlighted materials research at the Army Research Laboratory (ARL). Reprint requests and downloads off the website have been at record-setting paces. It is gratifying to see the collective six-month effort of so many people, both at ARL and at AMPTIAC, be so well-received.

We take great pride in providing our readership with timely and informative articles which meet the highest standards of journalistic excellence and technical accuracy. Even so, errors do (albeit infrequently) make it to print, despite our best efforts. One such error in our last issue (v8, n4) was recently brought to our attention; on page 24 of the issue in Table 1. This table lists many of the major manufacturers of ceramic armor materials, and which material products they currently produce for armor applications. In the bottom third, the table fails (by omission) to list Cercom, Inc. as a manufacturer of hot-pressed Silicon Carbide (SiC). In fact, Cercom has been one of the world's largest manufacturers of SiC for many years. We apologize for this error and any misperceptions it may have caused among our readers. In response, we have corrected this omission in the on-line version of the Quarterly (downloadable in PDF format via our website). For those who have a particular interest in ceramic materials or ceramic armor applications, we would recommend that you consider downloading a new and correct version for your records.

Thank you for your continued support. - Editor

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John W. Lincoln Award Presented

Mr. Robert P. Bell, who retired from Lockheed Martin Aeronautics Company in July 2003, was presented the 2004 John W. Lincoln Award. It was given in recognition of his outstanding work during his 37 year career with Lockheed Martin in advancing technology associated with aircraft structural integrity. At the time of his retirement, he was the group supervisor and technical lead for the C-141 Aircraft Structural Integrity (ASIP) Group. He is credited with leading the work to successfully apply the concepts of risk analysis as developed by Dr. Lincoln to a number of critical C-141 problems, which enabled the aircraft to continue to fulfill its missions during periods of increased airlift requirements caused by crises such as Desert Storm, which interrupted normal aircraft maintenance and inspection. Since his retirement from Lockheed Martin, he consults in the area of aircraft structural integrity with CACI International. The Award was presented at the 2004 USAF Aircraft Structural Integrity Program (ASIP) Conference in Memphis, Tennessee on 30 November 2004. The Award, which consists of a gold medal and a certificate of recognition, was named in honor of the late Dr. John W. (Jack) Lincoln of the Aeronautical Systems Center, Wright-Patterson Air Force Base, Ohio. Dr. Lincoln was a pioneer and major contributor to the development and application of durability and damage tolerance design to insure the safety and longevity of both military and commercial aircraft. The Award has been presented previously to Dr. Lincoln (1996), to Mr. Charles Tiffany (1997), to Mr. Thomas Swift (1998), to Professor Jaap Schijve (1999), to Professor Alten Grandt, Jr. (2000), to Dr. James Newman (2001), to Mr. Royce Forman (2002) and to Mr. Ward Rummel (2003). A plaque with the names of the recipients is on display during the ASIP Conference and then at Wright-Patterson Air Force Base, Ohio.

GENERLY GUARTERLY

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