THE INFLUENCE OF METALLURGY ON MICROBIOLOGICALLY INFLUENCED CORROSION

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ABSTRACT

In the study of microbiologically influenced corrosion (MIC) of metals there is an interrelationship between the metallurgical character and composition, the electrolyte, and bacterial species. Basic mechanisms of MIC, examples, and influence of metallurgical factors are reviewed.

INTRODUCTION

Microbial biofilms develop on all surfaces in contact with aqueous environments. Chemical and electrochemical characteristics of a metal substrate influence the formation rate and cell distribution of microfouling films in seawater during the first hours of exposure. Electrolyte concentration, pH, and inorganic ions affect microbial settlement.

Cells within biofilms grow, reproduce and form colonies that are physical anomalies on a metal surface; local anodes and cathodes and the formation of differential aeration cells result. Under aerobic conditions, areas under respiring colonies become anodic and surrounding areas become cathodic. A mature biofilm prevents diffusion of oxygen to cathodic sites and the diffusion of aggressive anions, such as chloride, to anodic sites. Outward diffusion of metabolites and corrosion products is also impeded. If areas within the biofilm become anaerobic the cathodic mechanism changes and may be shifted to the reduction of water or microbiologically produced H₂S.¹

The term microbiologically influenced corrosion is used to designate corrosion resulting from the presence and activities of microorganisms within biofilms. Reactions within biofilms are localized and basic microbial reactions related to MIC in metals include the following: 1) sulfide production, 2) acid production, 3) ammonia production, and 4) metal deposition.

Resistance to and prevention of MIC must be considered in overall engineering design and choice of materials for specific applications. Composition, preparation and heat treatments influence resistance. Metal surface microtopography, including cracks, crevices and roughness, affects attachment of microorganisms. Susceptibility of weld, bend and joint fabrication areas to MIC has been frequently demonstrated. Porous welds provide increased sites for colonization. This paper will review the influence of metallurgy on MIC.

METALLURGY AND CASE STUDIES

Metals listed as commercially pure actually contain a variety of impurities and imperfections which influence corrosion. In general, as purity increases, the tendency for a metal to corrode reduces
proportionately. However, high purity metals frequently have low mechanical strength, leading to the use of alloying elements to improve mechanical, physical, fabrication and corrosion characteristics. Metal composition and manufacturing specifications influence susceptibility to MIC. Following are case histories for several metals and alloys where MIC has been reported.

A. Ferrous Alloys

1. Iron and Mild Steel

MIC has been reported for mild steel piping and equipment exposed in the marine environment, soil, oil refining industry, fossil fuel and nuclear power plants and process industries. Sanders and Hamilton analyzed microbial corrosion in North Sea oil exploration. Sulfate-reducing bacteria (SRB), sulfur-oxidizing bacteria (SOB), hydrocarbon-oxidizing bacteria, iron-oxidizing bacteria, slime-forming bacteria and fungi were identified as causing corrosion. The authors defined two distinct forms of SRB mediated corrosion:

1) pitting caused by SRB growing in the biofilm on metal surfaces, and
2) sulfide-induced stress corrosion cracking (SCC), hydrogen induced cracking or blistering caused by hydrogen permeation in high dissolved sulfide conditions.

Pope et al. reported that organic acids (acetic, formic and lactic acids) produced by bacteria caused corrosion of a buried carbon steel pipeline. Dias and Bremer investigated a leaking undersea carbon steel pipeline after operation for five years and found that corrosive attack was confined to low areas where water accumulated inside the pipe. Pitting was attributed to microbiologically produced acids under bacterial deposits. SRB did not play a role as evidenced by the lack of FeS in the pits and absence of SRB.

Bibb described failure of mild steel pipework handling raw water, an epoxy-lined seawater cooling pipe and galvanized hot water pipework. The presence of the organism Desulfovibrio desulfuricans, an SRB, was confirmed in all failures. Pope showed that acid-producing bacteria were the primary cause of MIC of carbon steel piping, tanks and water boxes. In general, carbon steels are not exposed in practical applications without cathodic protection, protective coatings or a combination of both methods of corrosion protection.

2. Stainless Steels

The corrosion resistance of stainless steels (SS) is due to the formation of a thin passive chromium-iron oxide film at or above additions of Cr in amounts of 12% or more. Passivity can break down under the following, usually localized, environments:

a) Dilute and concentrated HCl, HBr and HF and salts that hydrolyze these acids.
b) Oxidizing chlorides such as FeCl₃, CuCl₂ or NaOCl.
c) Seawater, except for brief exposures or when cathodically protected.
d) Some organic acids including oxalic, lactic and formic acids.

Additionally, formation of HCl and heavy metal chlorides may result.

Metal-depositing organisms, important in MIC of stainless steels, may catalyze the oxidation of metals, accumulate abiotically oxidized metal precipitates, or derive energy by oxidizing metals. The dense deposits of cells and metal ions create oxygen concentration cells that effectively exclude oxygen from the area immediately under the deposit. Underdeposit corrosion is extremely important because it initiates a series of events that are, individually or collectively, extremely corrosive. Figure 1 shows reactions possible under tubercles created by metal-depositing bacteria. In an oxygenated environment, the area immediately under the deposit is deprived of oxygen. That area becomes a relatively small anode compared to the large surrounding oxygenated cathode. Cathodic reduction of oxygen may result in an increase in pH of the solution in the vicinity of the metal. The metal will form metal cations at anodic sites.
If the metal hydroxide is the thermodynamically stable phase in the solution, the metal ions will be hydrolyzed by water with the formation of H⁺ ions. If the cathodic and anodic sites are separated from one another, the pH at the anode will decrease and that at the cathode will increase. The pH within the anodic pit depends on specific hydrolysis reactions. The lowest pH values are predicted for alloys containing chromium and molybdenum. For this reason, underdeposit attack is particularly aggressive on stainless steels. In addition, Cl⁻ ions from the electrolyte will migrate to the anode to neutralize any buildup of charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, pitting involves the conventional features of differential aeration, a large cathode: anode surface area and the development of acidity and metallic chlorides. These environments also harbor obligately anaerobic SRB and acid-producing bacteria.

A persistent problem with the use of stainless steels is their susceptibility to crevice corrosion. Many cases of MIC of stainless steels have been explained as the formation of crevices by bacterial deposits. The presence of a biofilm is reported to shift the corrosion potential in the positive direction into the range of the pitting potential. Landrum discussed crevice corrosion of stainless steels resulting from faulty design. The crevice area, usually small compared to the large cathodic surrounding area, will become the anode.

One of the most common forms of MIC attack in austenitic SS is in the form of pitting at or adjacent to welds—at the heat affected zone, the fusion line and in the base metal (Fig. 2). Borenstein made the following observations after extensive studies of MIC in 304L (18% Cr, 9% Ni, .03% C, bal. Fe) and 316L (17% Cr, 12% Ni, 2.5% Mo, .03% C, bal. Fe) weldments: both austenite and delta ferrite phases may be susceptible; combinations of filler and base materials have failed, including matching, higher and lower alloyed filler combinations; and solution annealing and pickling may produce welds that are less susceptible. A
and 316SS. \( \text{Fe}^{3+} \) and \( \text{Mn}^{4+} \) produced by bacteria combined with \( \text{Cl}^- \) to form corrosive solutions. Pitting was concentrated almost exclusively at weld seams. Pope et al.\(^6\) described several similar case studies in fossil fuel and nuclear power generating plants. Similarly, Puckorius\(^{16}\) described the sudden failure of 304SS condenser tubes at an electric utility. The authors attribute many of the failures to hydrotest procedures during which naturally occurring water was introduced into piping systems to test the integrity of the welds. After hydrotesting, systems may not be effectively drained, leaving stagnant or low-velocity conditions for weeks or months at temperatures favorable to the establishment and growth of microbiological colonies. In one case, a 304SS pipeline designed for a 30-year lifetime failed when put into freshwater service 15 months after hydrotesting. Stoecker and Pope\(^7\) identified an aerobic Bacillus as the cause of weld failures in a 304SS tank used to store hot demineralized water. Bacterial deposits were associated with large transgranular pits typical of chloride SCC. This observation demonstrates that using demineralized water for hydrotesting will not prevent MIC.

Scott and Davies\(^8\) documented MIC in an austenitic 904L stainless steel (20% Cr, 25% Ni, 4.5% Mo, 1.5% Cu, 0.02 max. C, bal. Fe) used in a tube and shell heat exchanger for cooling sulfuric acid in brackish and seawater applications. The failure occurred within two weeks of startup and was accompanied by attack of welds and crevice corrosion. This appeared to be the result of underdeposit corrosion induced by metal-depositing bacteria and SRB.

Recent reports of MIC related to 6% Mo stainless steels have been reported in laboratory experiments. Little et al.\(^9\) observed deep etching of SMO254 SS (20% Cr, 18% Ni, 6.5% Mo, 0.75% Cu, 0.2% N, bal. Fe) after exposure to an iron/sulfur-oxidizing mesophilic bacterium and also to a thermophilic mixed SRB culture. No MIC was observed, however, under similar exposure for AL6XN SS, also a 6% Mo SS (21% Cr, 24.5% Ni, 6.5% Mo, 1.047...
0.2% N, bal. Fe). Scott and Davies \( ^{20} \) reported laboratory evidence of MIC for both AL6XN and SMO254 SS.

**B. Copper Alloys**

Copper alloys are frequently used for seawater piping systems and heat exchangers due to their good corrosion resistance combined with mechanical workability, excellent electrical and thermal conductivity, ease of soldering and brazing, and resistance to macrofouling. In oxygenated seawater a film of cuprous oxide, cuprite \((\text{Cu}_2\text{O})\), forms on copper alloys. Copper ions and electrons pass through the film. In chloride-containing waters, copper ions dissolve and precipitate as \( \text{Cu}_2(\text{OH})_3\text{Cl} \), independent of alloy chemistry. Alloying nickel and small amounts of iron into copper improves the corrosion resistance. CDA 706 (88.5% Cu, 10% Ni, 1.5% Fe) has been shown to be the most corrosion resistant copper alloy for seawater service. \( ^{21} \)

Copper alloys are vulnerable to biocorrosion. Differential aeration, selective leaching, underdeposit corrosion and cathodic depolarization have been reported as mechanisms for MIC of copper alloys. Pope et al. \( ^{22} \) proposed that the following microbial products accelerate localized attack: \( \text{CO}_2 \), \( \text{H}_2\text{S}, \text{NH}_3 \), organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides and disulfides. Geesey et al. \( ^{23} \) demonstrated that extracellular polymers produced by bacteria play a role in the corrosion of copper alloys.

In the presence of waterborne sulfides, copper alloys form a porous layer of cuprous sulfide with the general stoichiometry \( \text{Cu}_2\text{xS}, \text{O}\text{c}\text{x}<1 \). Copper ions migrate through the layer, react with more sulfide, and produce a thick black scale. It has been argued that if the copper sulfide layer were djurelite \((\text{Cu}_1.96\text{S})\), the sulfide layer would be protective. Even if such a sulfide film were technically passivating, the film’s mechanical stability is so poor that sulfide films are useless for corrosion protection. McNeil et al. \( ^{24} \) reported that sulfide corrosion products on 99Cu were consistently non-adherent, while those on 90/10 and 70/30 CuNi were adherent in SRB laboratory cultures and in natural waters. In the presence of turbulence, the loosely adherent sulfide film is removed, exposing a fresh copper surface to react with sulfide ions. For these reasons turbulence-induced corrosion and sulfide attack of copper alloys cannot easily be decoupled. Transformations between sulfides or conversions of sulfides to oxides result in changes in volume that weaken the attachment scale and oxide subscale leading to spalling. Bared areas repassivate, forming cuprous oxide.

The composition of copper alloys influences the rate of biofilm formation and the rate of sulfide derivatization. For example, alloys containing more nickel foul at a faster rate than do the alloys containing a higher percentage of copper. Furthermore, metals in the alloy which complex easily with sulfides are found in the mineral of the corrosion product. In Cu/Ni the copper will react with sulfides much faster than the nickel. In practice, nickel minerals are not found in the sulfide corrosion products on Cu/Ni alloys. \( ^{25} \)

Thick surface deposits and depletion of nickel in pits of 90/10 Cu/Ni were observed in the presence of SRB in a seawater piping system after one year of service. \( ^{26} \) Intermittent periods of flow and stagnation had occurred during the shipbuilding process. Figure 3a shows surface deposits and pitted areas. Figure 3b is a cross section through a pit, exposing subsurface bacteria. If copper nickel is used in an acid deoxygenated environment, the nickel will be dissolved and the copper will become more noble. Wagner et al. \( ^{27} \) described dealloying of nickel in 70/30 Cu/Ni exposed to flowing natural seawater. Figure 4 shows 99% Cu granules found within pits after removal of biofilm.

Little et al. \( ^{28} \) reported localized corrosion in field and laboratory studies of welds and heat-affected zones in Cu/Ni seawater piping systems exposed to estuarine water and seawater. This was due to metal segregation during heating processes.
formation of anaerobic niches within the biofilm for settlement of SRB, and production of sulfides at the weld seam surface. Exposure of sulfide-derivatized surfaces to fresh, aerated seawater results in rapid spalling on the downstream side of weld seams. Bared surfaces become anodic to the sulfide-coated weld root, accelerating corrosion.

Pope documented MIC of 90/10 Cu/Ni, admiralty and aluminum brass, and welded aluminum bronze at electric generating facilities using fresh or brackish cooling waters. Most of the Cu/Ni tubes had underdeposit corrosion due to the formation of deposits by slime-forming organisms in association with iron- and manganese-depositing bacteria. Ammonia-producing bacteria were isolated from scale and organic material on the admiralty brass tubes suffering ammonia-induced SCC.

C. Nickel Alloys

Nickel alloys, such as Monel 400 (66.5% Ni, 31.5% Cu, 1.25% Fe) have been used extensively in highly aerated fast-moving seawater environments as evaporators, heat exchanger pumps and valves, diffusers for steam nozzles in steam ejectors and turbine blades. Friend reported that a passive film similar in structure to that observed on pure nickel is formed on Ni-Cu alloys containing more than 30% Ni. Ni alloys containing less than this amount behave like copper. The formation of the
protective film on nickel is aided by the presence of iron, aluminum and silicon. Uhlig and Revie calculated that a critical nickel concentration of 35% was required for passivity. In high velocity seawater, nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under highly turbulent and erosive conditions.

Monel 400 is susceptible to pitting and crevice corrosion attack under stagnant conditions where chlorides penetrate the passive film at weak points. Sulfides can cause either a modification or breakdown of the oxide layer. Schumacher reported that Monel 400 was susceptible to underdeposit corrosion and oxygen concentration cells formed by bacteria. Gouda et al. demonstrated pitting of Monel 400 tubes exposed in Arabian Gulf seawater where pits developed underdeposits of SRB and nickel was selectively dealloyed. Little et al. reported selective dealloying in Monel 400 in the presence of SRB from an estuarine environment.

Pope reported a case study from nuclear power plants in which severe pitting corrosion was observed under discrete deposits on Monel heat exchanger tubes. The deposits formed by Fe- and Mn-depositing bacteria in association with SRB contained large amounts of Fe and Cu, significant amounts of Mn and Si and reduced amounts of Ni. No evidence for MIC in Ni – Cr (Inconel) and Ni – Cr – Mo (Hastelloy) has been reported. Hastelloy C (54% Ni, 15% Cr, 16% Mo, 4% W, 5% Fe) shows outstanding resistance to pitting or crevice attack in seawater.

D. Aluminum and Aluminum Alloys

The corrosion resistance of Al and its alloys is due to an aluminum oxide passive film that is 20 to 100 Å thick for air-formed films. Anodizing produces thicker insulating films and better corrosion resistance. The natural film on aluminum alloys can be attacked locally by halide ions such as chloride. The susceptibility of aluminum and its alloys to localized corrosion makes it particularly vulnerable to MIC. Most reports of MIC are for aluminum (99%), 2024 and 7075 alloys used in aircraft or in underground fuel storage tanks. Localized corrosion attributed to MIC occurs in the water phase of fuel-water mixtures in the bottom of tanks and at the fuel-water interface. Contaminants in the fuel including surfactants, water, and water soluble salts encourage growth of bacteria. Two mechanisms for MIC of aluminum alloys have been documented: production of water soluble organic acids by bacteria and fungi, and formation of differential aeration cells.

Schmitt reported severe MIC of a finned Al alloy heat exchanger after several months exposure to potable water. Metallographic examination of corrosion sites showed cubic pitting indicative of an acid-chloride attack. Additional problems due to MIC were reported for aluminum screens in a solar energy system covered with a biofilm.

Aluminum-magnesium alloys (5000 series) used for marine applications resist uniform corrosion, however some are susceptible to pitting, intergranular attack, exfoliation and SCC. Crooker observed that biofilm formation in natural seawater may play a role in the basic mechanism of crack formation.

E. Titanium and Titanium Alloys

There are no case histories that document MIC of titanium and its alloys. Because of the extremely high standard free energy of formation, the production of titanium sulfide in the presence of a biofilm is unlikely. Schutz reviewed mechanisms for MIC and titanium's corrosion behavior under a broad range of conditions. He concluded that at temperatures below 100°C titanium is not vulnerable to SOB, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells and hydrogen embrittlement. In laboratory studies, Little et al. did not observe MIC in the presence of SRB or iron oxidizing/SOB at mesophilic (23°C) or thermophilic (70°C) temperatures.
CONCLUSIONS

MIC is a localized corrosion documented to be a factor in failures of engineering materials. Alloy composition, surface finish and heat treatments influence the rate of biofilm formation and MIC. Surface preparations, welds and fabrication designs should avoid sites for microbiological attachment and growth. To reduce susceptibility, construction design must consider suitable metals and alloys and their preparation for specific applications.

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Biofouling, corrosion, biodeterioration, electrochemistry