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Alloying elements are added to metals to improve workability, electrical properties, and corrosion resistance. Alloying elements also alter the formation, chemical composition, thickness, and tenacity of corrosion products and may increase or decrease susceptibility to microbiologically influenced corrosion (MIC). The influence of alloying elements on MIC are reviewed for stainless steels and copper, nickel, aluminum, and titanium alloys.

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Impact of Alloying on Microbiologically Influenced Corrosion—A Review

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Alloying elements are added to metals to improve workability, electrical properties, and corrosion resistance. Alloying elements also alter the formation, chemical composition, thickness, and tenacity of corrosion products and may increase or decrease susceptibility to microbiologically influenced corrosion (MIC). The influence of alloying elements on MIC are reviewed for stainless steels and copper, nickel, aluminum, and titanium alloys.

Microbiological biofilms develop on all surfaces in contact with aqueous environments. Chemical and electrochemical characteristics of a metal substratum influence the formation rate and cell distribution of micro-fouling films in seawater during the first hours of exposure. Electrolyte concentration, pH, and organic and inorganic ions also affect microbiological settlement. Biofilms produce an environment at the biofilm/metal interface that is radically different from that of the bulk medium in terms of pH, dissolved oxygen, and inorganic and organic species. Reactions within biofilms can control corrosion rates and mechanisms.

The term "microbiologically influenced corrosion (MIC)" is used to designate corrosion caused by the presence and activities of microorganisms within biofilms. The reactions are usually localized and can include: (1) sulfide production, (2)

acid production, (3) ammonia production, (4) metal deposition, and (5) metal oxidation and reduction.

Copper Alloys

Copper alloys are used frequently for seawater piping systems and heat exchangers due to 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 (Cu_2O), forms on copper alloys. Copper ions and electrons pass through the film. 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 increases resistance to turbulence-induced corrosion.

Copper alloys are vulnerable to biocorrosion. Differential aeration, selective leaching, underdeposit cor-

rosion, and cathodic depolarization have been reported as mechanisms for MIC of copper alloys. Pope et al. proposed that the following microbiological products accelerate localized attack: carbon dioxide, hydrogen sulfide, and ammonia (CO_2 , H_2S , NH_3), organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides, and disulfides.¹

In the presence of sulfides, copper alloys form a porous layer of cuprous sulfide with the general stoichiometry $\text{Cu}_x\text{-xS}$, $0 < x < 1$. Copper ions migrate through the layer, react with more sulfide, and produce a thick black scale. McNeil and Odom described a model that predicts sulfide-induced corrosion in the presence of sulfate-reducing bacteria (SRB).² The authors concluded that if the reaction of metal oxide with sulfide has a negative standard free energy of reaction, SRB-related MIC will occur. If the reaction has a positive standard free energy of reaction, this form of corrosion will not occur. Negative standard free energies of reactions were used to predict SRB-MIC for copper alloys. Analysis of sulfide corrosion products recovered from corroding copper alloys confirmed the prediction.

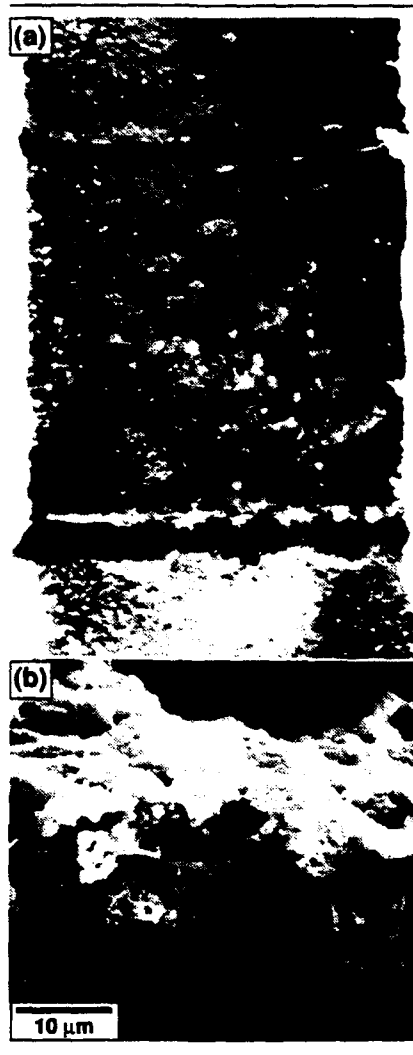


FIGURE 1

(a) Pitted 90/10 copper/nickel seawater piping after one year in service and (b) bacteria in cross section of pitted area.

Specific copper sulfides have been suggested as characteristic of SRB sulfide production. Chalcocite (Cu_2S) and covellite (CuS_{1-x}) are frequently identified in copper corrosion products associated with SRB.³ Djurleite ($\text{Cu}_{31}\text{S}_{16}$) formation has been reported for copper/nickel alloys.

It has been argued that if the copper sulfide layer were djurleite, 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. reported that sulfide corrosion products on unalloyed copper (UNS C11000) were consistently non-adherent, while those on 90/10 (UNS

C70610) and 70/30 (UNS C71500) copper/nickel were adherent in SRB laboratory cultures and in natural waters.³

Nickel minerals have not been found in corrosion products on 90/10 or 70/30 copper/nickel alloys. Selective dealloying of zinc, nickel, and iron from copper alloys has been reported by several investigators. Little et al.⁴ demonstrated dealloying of nickel from 90/10 copper/nickel in association with SRB (Figure 1). Wagner et al. described dealloying of nickel in 70/30 copper/nickel exposed to flowing natural seawater.⁵

SRB are not necessary for MIC-induced pitting of copper alloys. While the role of the biofilm in copper pitting is not entirely clear, it appears that the presence of the biofilm contributes to corrosion by maintaining enhanced local chloride concentrations and differential aeration cells. Pope documented MIC of 90/10 copper/nickel, admiralty brass (UNSC44300), aluminum brass (UNS C68700), and welded aluminum bronze at electric generating facilities using fresh or brackish cooling waters.¹ Most of the copper/nickel tubes had underdeposit corrosion due to 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 stress corrosion cracking.

Nickel Alloys

Nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under turbulent and erosive conditions. Nickel alloys are used extensively in highly aerated, high-velocity seawater applications. Uhlig and co-workers calculated that a critical nickel concentration of 35 percent was required for passivity. Nickel/copper alloys containing less than this amount behave like copper.⁶ The formation of the protective film on nickel is aided by the presence of iron, aluminum, and silicon.

Alloy 400 (UNS N04400) is susceptible to pitting and crevice corrosion attack where chlorides penetrate the passive film. Sulfides can cause either a modification or breakdown

of the oxide layer. Schumacher reported that alloy 400 was susceptible to underdeposit corrosion and oxygen concentration cells formed by bacteria.⁷ Gouda et al. demonstrated localized corrosion of alloy 400 tubes exposed in Persian Gulf seawater where pits developed under deposits of SRB and nickel was selectively dealloyed.⁸ Pope reported a case study from nuclear power plants in which severe pitting corrosion associated with dealloying was observed under discrete deposits on alloy 400 heat exchanger tubes.¹ Deposits formed by iron- and manganese-depositing bacteria in association with SRB contained large amounts of iron and copper, significant amounts of manganese and silicon, and reduced amounts of nickel. No evidence for MIC in nickel-chromium alloys (such as alloy 600 [UNS N06600]) and nickel-chromium-molybdenum alloys (such as alloy C-276 [UNS N10276]) has been reported.

Stainless Steels

The corrosion resistance of stainless steels (SS) is due to the formation of a thin passive chromium-iron oxide film at additions of chromium in amounts of 12% or more. Metal-depositing organisms, important in MIC of SS, may catalyze the oxidation of metals, accumulate abiotically oxidized metal precipitates, or derive energy by oxidizing metals. 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 important because it initiates a series of events that are, individually or collectively, extremely corrosive. In an oxygenated environment, the area immediately under the deposit becomes a relatively small anode compared to the large surrounding 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, metal ions will be hydrolyzed by water with formation of H^+ ions. If cathodic and anodic sites are separated from one another, the pH at the anode will decrease and that at the cathode will



FIGURE 2

Cross section showing pitting at a weld of type 316L SS base metal and 308L SS filler metal (5x).⁹

increase. The pH within anodic pits depends on specific metal hydrolysis reactions. The lowest pH values are predicted for alloys containing chromium and molybdenum.

One of the most common forms of MIC attack in type 300 series austenitic SS (AUSS) is pitting at or adjacent to welds at the heat-affected zone (HAZ), the fusion line, and in the base metal (Figure 2). Borenstein made the following observations for MIC in SS weldments: both austenite and delta ferrite phases may be susceptible; and all combinations of filler and base materials have failed, including matching, higher- and lower-alloyed filler combinations.⁹ Microsegregation of chromium and molybdenum with chemically depleted regions increases susceptibility to localized attack.¹⁰

Stainless steels containing 6% or more molybdenum, often called superaustenitic SS, were once thought to be immune to MIC because molybdenum increases the resistance of AUSS to chloride and acid solutions. However, Scott et al.¹ documented MIC in laboratory testing of UNS S31254 and UNS N08366, both containing about 6.5% molybdenum.¹¹ Little et al. observed deep etching of S31254 after exposure to both an iron/sulfuroxidizing mesophilic bacterium and a thermophilic mixed-SRB culture (Figure 3).¹²

No discussion of MIC of SS would be complete without some reference to ennoblement. Ennoblement of corrosion potential (E_{corr})

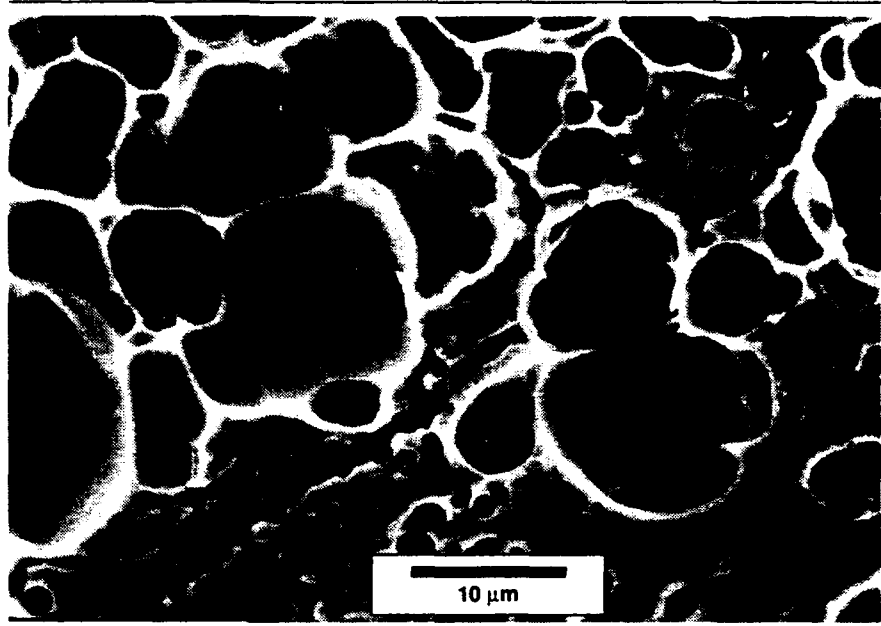


FIGURE 3

Pitted UNS S31254 after 75-day exposure to mesophilic iron/sulfur-oxidizing bacteria.

during exposure to natural seawater has been reported by several investigators. The practical importance of ennoblement is increased probability of localized corrosion as E_{corr} approaches the pitting potential (E_{pit}) for SS vulnerable to crevice corrosion, especially types 304 (UNS S30400) and 316 (UNS S31600). Sustained ennoblement does not indicate corrosion but persistence of passivity. At the onset of localized corrosion, E_{corr} moves from noble to active regions. Ennoblement has also been reported for SS containing 6% molybdenum and other corrosion-resistant materials. Johnsen and Bardal reported that E_{corr} approached -50 mV (vs saturated calomel electrode [SCE]) after 28 days for SS containing 1 to 3% molybdenum, and 50 to 150 mV (SCE) for SS containing 6% molybdenum in the same time period.¹³

Aluminum and Aluminum Alloys

The corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film. Anodizing produces thicker insulating films and better corrosion resistance. The natural film on aluminum alloys can be attacked locally by halide ions. The susceptibility of aluminum and its alloys to localized corrosion makes it particularly vulnerable to MIC. Most reports of MIC

are for aluminum (99%) and UNS A92024 and UNS A97075 alloys used in aircraft or 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.¹⁴ Contaminants in 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.

Titanium and Titanium Alloys

There are no case histories of MIC for titanium and its alloys. Schutz reviewed mechanisms for MIC and titanium's corrosion behavior under a broad range of conditions.¹⁵ He concluded that at temperatures below 100°C, titanium is not vulnerable to iron/sulfur-oxidizing bacteria, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells, and hydrogen embrittlement. In laboratory studies, Little et al. did not observe any corrosion of grade 2 (UNS R50400) titanium in the presence of SRB or iron/sulfur oxidizing bacteria at mesophilic (23°C) or thermophilic (70°C) temperatures.¹² Using the model of McNeil and Odom,

one would predict that titanium would be immune to SRB-induced corrosion.² There are no standard free energy reaction data for the formation of a titanium sulfide. If one assumes a hypothetical sulfide product to be titanium sulfide, the standard enthalpy of reaction is +587 kJ. While standard free energies of reaction are not identical to standard enthalpies of reaction, it is still unlikely that titanium will be derivatized to the sulfide under standard conditions of temperature and pressure.

Summary

MIC is localized corrosion and has been documented in failures of copper, nickel, ferrous, and aluminum engineering materials. The primary effect of alloying elements is to stabilize a protective film either mechanically or chemically. Additions of nickel and iron improve the mechanical properties of copper alloys but may increase susceptibility to MIC. Chromium and molybdenum additions as high as 20 and 6%, re-

spectively, to stainless steels do not impart immunity to MIC. No cases describing MIC of titanium have been reported.

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