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1. Agency Use star, secure starting.		3. Report Type a	and Dates Covered.	
	December 1993	Final - Proce	edings	
4. Title and Subtitie.			5. Funding Numbers.	
Microbiologically Influenced Corro	ision in Offshore Oil and G	as Systems	Project No. 03103	
6. Author(s).			Task No 200	
Brenda Little and Patricia Wagner	,	-10	Accession No DN094463	
	1	ntiv	Work Unit No. 573505204	
7. Performing Organization Name(s) a Naval Research Laboratory Ocean Sciences Branch Steppis Space Contor, MS 20520	and Address(cs).	E JAN 28 1994	8. Performing Organization Report Number. NRL/PP/733393-0020	
Stennis Space Center, MS 33323	-5004	E E		
9. Sponsoring/Monitoring Agency Nar	me(s) and Address(es).		10. Sponsoring/Monitoring Agency	
Naval Research Laboratory Report Number. Operations Research and Strategic Planning NRL/PP/733393-0020 Stennis Space Center, MS 39529-5004 NRL/PP/733393-0020				
Published in New Orleans Offshor 12a. Distribution/Availability Statemen Approved for public release; distri	re Corrosion Conference F nt. bution is unlimited.	Proceedings.	12b. Distribution Code.	
13. Abstract (Maximum 200 words). Stainless steels, copper/nickel added to metals to improve workat chemical composition, thickness a cally influenced corrosion (MIC).	and titanium alloys are fre pility, electrical properties a and tenacity of corrosion pre	equently used in offsho Ind corrosion resistance oducts and may increas	re and gas systems. Alloying elements ar Alloying elements also alter the formation e or decrease susceptibility to microbiolog	
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New Orleans OFFSHORE **CORROSION CONFERENCE**



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Proceedings

December 2/3, 1993



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Microbiologically Influenced Corrosion in Offshore Oil and Gas Systems

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ABSTRACT

Stainless steels, copper/nickel and titanium alloys are frequently used in offshore oil and gas systems. 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).

INTRODUCTION

Microbial 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 microfouling films in seawater during the first hours of exposure. Electrolyte concentration, pH, organic and inorganic ions also affect microbial 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.¹ Reactions within biofilms can control corrosion rates and mechanisms. The term microbiologically influenced corrosion (MIC) is used to designate corrosion resulting from 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, as well as, 5) metal oxidation and reduction.

COPPER AND NICKEL 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 (Cu₂O), forms on copper alloys. Copper ions and electrons pass through the film. Copper ions dissolve and precipitate as Cu₂(OH)₃Cl, independent of alloy chemistry. Alloying nickel and small amounts of iron into copper results in a single phase structure and increases resistance to turbulence induced corrosion. CDA 706 (88.5% Cu, 10% Ni, 1.5% Fe) has been shown to be the most corrosion resistant copper alloy for seawater service.²

Copper alloys are vulnerable to MIC. Differential aeration, selective leaching, underdeposit corrosion and cathodic depolarization have been reported as mechanisms for MIC of copper alloys. Pope et al.³ proposed that the following microbial products accelerate localized attack: CO_2 , H_2S , NH_3 , organic and inorganic acids; metabolites that act as depolarizers; and sulfur compounds such as mercaptans, sulfides and disulfides. In the presence of sulfides, copper alloys form a porous layer of cuprous sulfide with the general stoichiometry Cu₂-xS, O<x<1. Copper ions migrate through the layer, react with more sulfide, and produce a thick black scale (Figure 1). McNeil and Odom⁴ described a model that predicts sulfide-induced corrosion in the presence of sulfate-reducing bacteria (SRB). Corrosion is initiated by sulfide-tich reducing conditions in the biofilm where the oxide layer is destabilized and acts as a source of metal-containing ions. The authors concluded that if any reaction of metal oxide with sulfide has a high negative standard free energy of reaction, SRB-related MIC will occur. If the reaction has a high positive standard free energy of reactions were used to predict SRB-MIC for copper alloys (Table 1). Analysis of sulfide corrosion products recovered from corroding copper alloys confirmed the prediction. Specific copper sulfides have been suggested as fingerprints for SRB sulfide production. Chalcocite (Cu₂S) and covellite (Cu₃₁S₁₆) 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.⁵ reported that sulfide corrosion products on 99 copper were consistently non-adherent, while those on 90/10 and 70/30 copper/nickel were adherent in SRB laboratory cultures and in natural waters.

Nickel minerals have not been found in corrosion products on 90/10 or 70/30 copper/nickel alloys.⁶ Selective dealloying of zinc, nickel and iron from copper alloys has been reported by several investigators.^{7,8} Little et al.⁸ demonstrated dealloying of nickel from a 90/10 copper/nickel in association with SRB. Wagner et al.⁷ described dealloying of nickel in 70/30 copper/nickel exposed to flowing natural seawater.

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.⁹ Pope¹⁰ documented MIC of 90/10 copper/nickel, admiralty and aluminum brass, and welded aluminum bronze at electric generating facilities using fresh or brackish cooling waters. 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. Mansfeld and Little reported that 5 copper alloys exposed to natural seawater were colonized by bacteria within 3 weeks, independent of alloy composition.¹¹ Corrosion rates were higher in natural seawater compared with artificial seawater for all copper alloys exposed (Table 2). Intergranular corrosion and denickelification of 70/30 copper/nickel was observed after 1 month (Figure 2).

Nickel alloys, including Monel 400 (66.5% Ni, 31.5% Cu, 1.25% Fe), are 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. Uhlig and co-workers¹² calculated that a critical nickel concentration of 35% was required for passivity. Nickel 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. 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 where chlorides penetrate the passive film. Sulfides can cause either a modification or breakdown of the oxide layer. Schumacher¹³ reported that Monel 400 was susceptible to underdeposit corrosion and oxygen concentration cells formed by bacteria. Gouda et al.¹⁴ demonstrated pitting of Monel 400 tubes exposed in Arabian Gulf seawater where pits developed under deposits of SRB and nickel was selectively dealloyed. Little et al.⁸ reported selective dealloying in Monel 400 in the presence of SRB from an estuarine environment (Figure 3).

Pope¹⁰ reported a case study from nuclear power plants in which severe pitting corrosion associated with dealloying was observed under discrete deposits on Monel heat exchanger tubes. 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.

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. Metaldepositing organisms, important in MIC of stainless steels, 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 (Figure 4). Underdeposit corrosion is important because it initiates a series of events that are, individually or collectively, extremely corrosive.¹⁵ In an oxygenated environment, the area immediately under the deposit becomes a relatively small anode compared to the large surrounding cathode (Figure 4). 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 increase. The pH within anodic pits depends on specific hydrolysis reactions (Table 3).¹⁶ The lowest pH values are predicted for alloys containing chromium and molybdenum.

One of the most common forms of MIC attack in austenitic SS is pitting at or adjacent to welds (Figure 5)¹⁷ at the heat affected zone, the fusion line and in the base metal. Borenstein¹⁸ made the following observations for 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 lack of sensitization in austenitic welds did not ensure protection. Additionally, surface conditions commonly associated with corrosion resistance, such as heat tint, and those related to residual stresses, including gouges and scratches, may increase susceptibility. Kearns and Borenstein¹⁹ state that welds having filler metal compositions matching the base metal have lower corrosion resistance than fully annealed base metal due to lack of homogeneity and the microsegregation of chromium and molybdenum. Chemically depleted regions can be much more susceptible to localized attack. Stein²⁰ reported that MIC susceptibility of base metal related to weld area was not related to sensitization but to the microstructure produced during the manufacturing process. Reannealing reduced the severity of the pitting corrosion. Videla et al.²¹ observed that sensitization heat treatments with related carbide precipitation

lowered pitting corrosion resistance of 304 and 410SS in the presence of SRB and aggressive anions.

Stainless steels containing 6% or more molybdenum were once thought to be immune to MIC because molybdenum increases the resistance of austenitic SS to chloride and acid solutions. However, Scott and Davies²² documented MIC in an austenitic 904L SS (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. Little et al.²³ observed deep etching of SMO254 SS (20% Cr, 18% Ni, 6.5% Mo, 0.75% Cu, 0.2% N, bal. Fe) after exposure to both an iron/sulfur-ogidizing mesophilic bacterium and a thermophilic mixed SRB culture (Figure 6).

Ennoblement of corrosion potential (E_{corr}) for stainless steels during exposure to natural seawater has been reported by several investigators.^{1,24,25} The practical importance of ennoblement is increased probability of localized corrosion as E_{corr} approaches the pitting potential (E_{pit}). Thermodynamic and kinetic factors have been discussed, including increase of the partial pressure of oxygen, a decrease in interfacial pH and organometallic catalysis. An increase of the partial pressure would move the reversible potential of the oxygen electrode in the noble direction, but cannot be used to explain large shifts in E_{corr}. A local decrease in pH would produce the same effect. Local acidification would move E_{pit} in the negative direction to potentials significantly below the reported E_{corr} values. Johnsen and Bardal²⁶ reported that E_{corr} approached -50 mV (vs saturated calomel electrode (SCE)) after 28 days for SS that contained 1-3 w/o molybdenum (Figure 7). In contrast, SS containing 6 w/o molybdenum reached values of +50-150 mV vs. SCE in the same time period. Early reports suggested that molybdenum was not found in the passive layer for alloys containing up to 5.2% molybdenum.²⁷ Recently, Olefjord and Wegrelius²⁸ studied the influence of molybdenum and nitrogen on the corrosion behavior of high alloyed SS containing 6% molybdenum. Passive layers contained 8-14% molybdenum. Since ennoblement is more pronounced for high molybdenum SS, molybdenum may play a role in the acceleration of the cathodic reaction leading to ennoblement of $E_{corr.}$

TITANIUM AND TITANIUM ALLOYS

There are no case histories of MIC for titanium and its alloys. Schutz²⁹ 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 iron/sulfuroxidizing bacteria, SRB, acid-producing bacteria, differential aeration cells, chloride concentration cells and hydrogen embrittlement. In laboratory studies, Little et al.²³ did not observe any corrosion of Grade 2 titanium in the presence of SRB or iron/sulfur oxidizing bacteria at mesophilic (23°C) or thermophilic (70°C) temperatures. Using the model of McNeil and Odom⁴ one would predict that titanium would be immune to SRB induced corrosion (Table 1). 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.

CONCLUSIONS

MIC is localized corrosion documented in failures of 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. Molybdenum found in the passive layer on stainless steel alloys may influence ennoblement of E_{corr} .

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research, Program Element 0601153N, through the NRL Defense Research Sciences Program. Approved for public release; unlimited distribution. NRL Contribution Number NRL/PP/7333--93-0020.

REFERENCES

1. B. Little, R. Ray, P. Wagner, Z. Lewandowski, W. C. Lee, W. Characklis, F. Mansfeld, Biofouling, 3, (1991): p. 45.

2. J. F. D. Bates, J. M. Popplewell, Corrosion, 32 8 (1975): p. 269.

3. D. H. Pope, D. J. Duquette, A. H. Johannes, P C. Wayner, Materials Performance, 23 4 (1984): p. 14.

4. M. B. McNeil, A. L. Odom, "Prediction of Sulfiding Corrosion of Alloys Induced by Consortia Containing Sulfate Reducing Bacteria (SRB)," International Symposium on Microbiologically Influenced Corrosion (MIC) Testing, (Miami, FL: ASTM, 1992).

5. M. B. McNeil, J. M. Jones, B. J. Little, Corrosion, 47 9 (1991): p. 674.

6. J. Jambor, private communication, 1990.

7. P. Wagner, B. Little, R. Ray, J. Jones- Meehan. "Investigations of Microbiologically Influenced Corrosion Using Environmental Scanning Electron Microscopy," CORROSION/92, paper no. 185, (Houston, TX: National Association of Corrosion Engineers, 1992).

8. B. Little, P. Wagner, R. Ray, M. McNeil, Marine Technology Society J. 24 3 (1990): p. 10.

9. H. H. Paradies, I. Hansel, W. Fischer, D. Wagner, "The Occurrence of a Severe Failure of Water Supplies in a County Hospital," International Copper Research Institute, Project No. 404 (1990).

10. D. H. Pope, Microbial Corrosion in Fossil-Fired Power Plants - A Study of Microbiologically Influenced Corrosion and a Practical Guide for its Treatment and Prevention, (Palo Alto, CA: Electric Power Research Institute, 1987).

11. F. Mansfeld, B. Little, Electrochimica Acta, 37 12 (1991): p. 2291.

12. H. H. Uhlig, W. R. Revie, Corrosion and Corrosion Control: an Introduction to Corrosion Science and Engineering, Third Edition, (NY, NY: Wiley-Interscience, 1985).

13. M. Schumacher, Seawater Corrosion Handbook, (Park Ridge, NJ: Noyes Data Corporation, 1979).

14. V. Gouda, I. Banat, W. Riad, S. Mansour, Corrosion, 49 1 (1993): p. 63.

15. L. L. Shreir (ed.), Corrosion, Vol. 1 & 2, Corrosion Control, (London, UK: Newnes-Butterworth, 1977).

16. T. P. Hoar, Disc. Faraday Soc., 1 (1947): p. 299.

17. G. Kobrin, Materials Performance, 15 7 (1976): p. 38.

18. S. W. Borenstein, Materials Performance, 30 1 (1991): p. 52.

19. J. Kearns, S. Borenstein, "Microbially Influenced Corrosion Testing of Welded Stainless Alloys for Nuclear Power Plant Service Water Systems," CORROSION/91, paper no. 279 (Houston, TX: National Association of Corrosion Engineers, 1991).

20 A. A. Stein, "Metallurgical Factors Affecting the Resistance of 300 Series Stainless Steels to Microbiologically Influenced Corrosion," CORROSION/91, paper no. 107 (Houston, TX: National Association of Corrosion Engineers, 1991).

21. H. A. Videla, M. F. L. deMele, D. A. Moreno, J. Ibars, C. Ranninger, "Influence of Microstructure on the Corrosion Behavior of Different Stainless Steels," CORROSION/91, paper no. 104 (Houston, TX: National Association of Corrosion Engineers, 1991).

22. P. J. B. Scott, M. Davies, Materials Performance, 28 5 (1989): p. 57.

23. B. Little, P. Wagner, R. Ray. "An Experimental Evaluation of Titanium's Resistance to Microbiologically Influenced Corrosion," CORROSION/92, paper no. 173 (Houston, TX: National Association of Corrosion Engineers, 1992).

24. S. C. Dexter, G. Y. Gao, Corrosion, 44 (1988): p. 717.

25. V. S. Scotto, R. Di Cintio, G. Marcenaro, Corrosion Science, 25 3 (1985): p. 185.

26. R. Johnsen, E. Bardal, Corrosion, 41 (1985): p. 296.

27. A. E. Yaniv, J. B. Lumsden, R. W. Staehle, J. Electrochemical Society, 124 4 (1977): p. 490.

28. I. Olefjord, L. Wegrelius, "Passivation of High Alloyed Stainless Steels," Symposium on Modifications of Passive Films (Paris, France, 1993).

29. R. W. Schutz, Materials Performance, 30 1 (1991): p. 58.

Table	1.	Standard	free	energies	of	reactions
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Cu2O + HS⁻ → Cu2S + OH⁻ Standard Free Energy of Reaction -110.2 kJ CuO + HS⁻ → CuS + OH⁻ Standard Free Energy of Reaction -103.2 kJ Fe3O4 + 4HS⁻ → 2FeS (pyrrhotite) + FeS2 + 4OH⁻ Standard Free Energy of Reaction -29.6 kJ TiO2 + HS⁻ → TiS + OH⁻ + 1/2 O2 Standard Enthalpy of Reaction +587 kJ ZrO2 + 2HS⁻ → ZrS2 + 2OH⁻ Standard Enthalpy of Reaction +206 kJ

Time (days)	Seawate ⁻	99Cu	90Cu:10Ni	70Cu:30Ni	Admiralty Brass	Aluminum Bronze
7	Natural	61.9	40.1	14.2	55.0	43.2
	Synthetic	46.8	30.6	9.1	39.9	27.2
29	Natural	45.2	15.2	20.7	41.0	22.7
	Synthetic	41.4	9.4	8.5	22.2	10.6

 Table 2. Corrosion rates for copper alloys (micrometers per year)

 Table 3. Specific hydrolysis reactions

Hydrolysis Reaction	Equilibrium pH
Fe ²⁺ + 2H ₂ O	pH = 6·64 – 1/2 log <i>a</i> _{Fe} 2+
Cr ³⁺ + 3H ₂ O ← Cr(OH) ₃ + 3H+	pH = 1·53 – 1/3 log <i>a</i> _{Cr} 3+
$Ni^{2+} + 2H_2O \rightleftharpoons Ni(OH)_2 + 2H^+$	pH = 6·5 – 1/2 log <i>a</i> _{Ni} 2+
Mo ³⁺ + 2H ₂ O ≓ MoO ₂ + 4H+ + e ⁻	pH* = (0·311 − 0·059 log a _{Mo} 3+ − <i>E</i>)/0·236
$Mn^{2+} + 2H_2O \rightleftharpoons Mn(OH)_2 + 2H^+$	pH = 1·53 – 1/3 log <i>a</i> _{Mn} 2+

 $E = -0.20 V (\nu. SCE)$



Figure 1. Black, porous corrosion layer on 90 Cu/10 Ni foil after exposure to SRB for 3 months (×3)



Figure 2. Pit interiors on 70 Cu/30 Ni showing intergranular corrosion. Arrows indicate grains of copper.



Figure 3. (a) Energy dispersive spectroscopy (EDS), (b) EDS spectrum of nickel alloy after exposure to estuarine water for six months showing accumulations of silicon, sulfur, and chlorine with elevated concentrations of iron and nickel, and (c) EDS spectrum of the residual metal in the base of the pit showing nickel depletion and copper enrichment.



Figure 4. Reactions possible in underdeposit corrosion.



Figure 5. (a) rust coloured streaks normal to weld seams in tank sidewall formed after 1 month of stagnant hydrotest water and (b) wet deposit of metal-depositing bacteria. Tubercule formation on 316L stainless steel (Ref. 17).



Figure 6. SS surface exposed to iron/sulfur oxidizing bacteria after 75 days.



Figure 7. Open circuit potential as function of time for six stainless steels exposed to flowing natural seawater (Ref. 26).