Biofouling and corrosion of stainless steels in natural waters

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Abstract The noble shift in corrosion potential to values between +300 and +400 mV_{SCE} and the accompanying increase in cathodic current density and polarization slope at mild cathodic potentials that develop during microbial colonization of passive metals, are collectively known as ennoblement. This phenomenon is of concern as the noble shift in the corrosion potential may lead to pitting corrosion. We have demonstrated, by growing pure cultures of manganese oxidizing bacteria (MOB) *Leptothrix discophora* SP-6 under well defined conditions, that microbial deposition of manganese oxides causes ennoblement of 316L stainless steel (SS). Exposing 316L corrosion coupons in lakes and streams supported this conclusion; the rate and extent of ennoblement were positively correlated with the rates of deposition and the amounts of biomineralized manganese oxides deposited on the surfaces of the SS corrosion coupons. X-ray photoelectron spectroscopy (XPS) analyses of the deposits from the ennobled coupons revealed a mixture of manganese oxides, as expected. Many natural waters can support growth of MOB. When manganese-oxidizing biofilms accumulate on surfaces of passive metals there is a potential for manganese redox cycling on the metal surface. This process is initiated by depositing minute amounts of manganese oxides on the metal surface. These microbially deposited manganese oxides are then reduced by the electrons derived from anodic dissolution of the metal; the metal is corroding and the manganese oxides are reduced to divalent manganese ions. However, since the manganese ions are liberated within the manganese-oxidizing biofilm, the manganese ions are immediately reoxidized, and the cycle continues.

Keywords Corrosion; corrosion of stainless steels; manganese-oxidizing bacteria; microbially influenced corrosion (MIC)

Introduction

Numerous researchers (Dickinson *et al.*, 1996; Little *et al.*, 1991; Scotto and Marcenaro, 1985) have shown that stainless steels, and other passive metals in natural waters exhibit a several-hundred mV increase in the corrosion potential accompanied by an increase in cathodic current drawn upon mild polarization of the samples. This phenomenon, termed ennoblement, has been observed in a wide variety of natural and engineered environments. Mattila *et al.* (1997) and Dexter and Gao (1988) described ennoblement in seawater, Dickinson *et al.* (1996) reported its occurrence in a fresh water stream and Linhardt (1994) described it in a hydroelectric power plant. Figure 1 uses one of our results to illustrate temporal changes in the corrosion potential of a 316 L stainless steel coupon immersed in a river.

Enoblement of stainless steels in natural waters may influence the material integrity; as the corrosion potential approaches the pitting potential, the material integrity may be compromised by localized (pitting and crevice) corrosion (Figure 2). This sequence of events, from an increase in corrosion potential to pit initiation, is well known to material scientists, although the microbial component is new.

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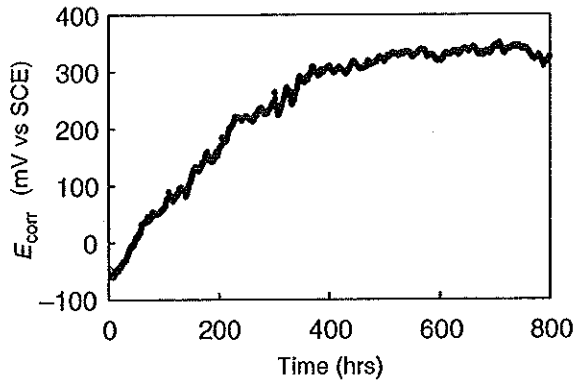


Figure 1 Temporal development of the corrosion potential, E_{corr}, of a 316 L stainless steel corrosion coupon immersed in a river (Dickinson *et al.* 1996)

Because pitting potential of 316L stainless steel in sea water is around 200 mV_{SCE}, the danger of pitting initiation in such an environment is serious. There are, however, reports of microbial involvement in pitting corrosion of stainless steels immersed in fresh waters of much lower chloride concentration than that found in sea water (Linhardt, 1994).

Mechanism of ennoblement

Several hypotheses have been postulated to explain the mechanism of ennoblement, each suggesting that it is caused by microbial colonization of the metal surface. Mollic and Trevis (1976) attributed ennoblement to microbially produced extracellular polymeric substances. Dexter and Gao (1988) suggested that acidification of the metal–biofilm interface caused by protons derived from the metabolic reactions in the biofilm increases the potential. Chandrasekaran and Dexter (1993) proposed a combination of acidification and hydrogen peroxide production. Eashwar and Maruthamuthu (1995) believed that ennoblement was caused by microbially produced passivating siderophores. Although many authors demonstrated the relationship between ennoblement and biofilm formation, the proposed hypothesis have not been supported by convincing experimental evidences to unequivocally demonstrate the mechanism of ennoblement.

Recent work has linked the ennoblement of SS to the microbially deposited manganese oxides on the surface of the metal (Dickinson and Lewandowski, 1996; Linhardt, 1996). We have demonstrated, in the laboratory and in the field, that stainless steels and other

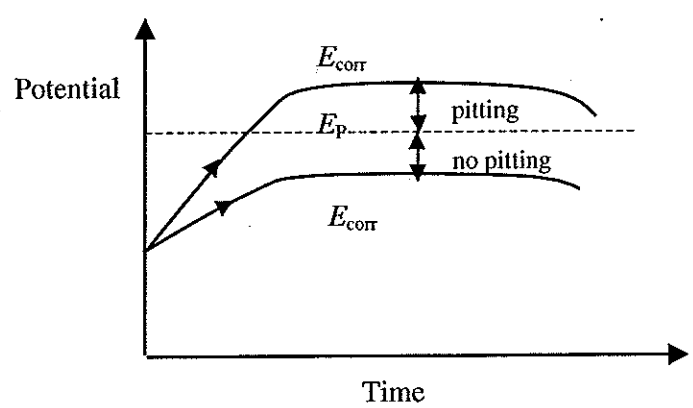


Figure 2 When the corrosion potential, E_{corr}, reaches the pitting potential, E_p, of the metal in the given solution, pits are initiated. This plots the relationship between the corrosion potential, pitting potential, and probability of pits initiation (from Sedrix, 1996)

passive metals ennoble when colonized by MOB (Dickinson *et al.*, 1996; Olesen *et al.*, 2000a,b). Because biomineralized manganese oxides are in direct electrical contact with the metal, the metal exhibits the equilibrium dissolution potential of the oxides described by the following reactions:

$$MnO_{2(s)} + H^+ + e^- \Rightarrow MnOOH_{(s)}\ E^0 = +0.81\ V_{SCE}\ E'_{pH=7.2} = +0.383\ V_{SCE} \quad (1)$$

$$MnOOH_{(s)} + 3H^+ + e^- \Rightarrow Mn^{2+} + 2H_2O\ E^0 = +1.26 V_{SCE}\ E'_{pH=7.2} = +0.336 V_{SCE} \quad (2)$$

This leads to the overall reaction:

$$MnO_{2(s)} + 4H^+ + 2e^- \Rightarrow Mn^{2+} + 2H_2O\ E^0 = +1.28 V_{SCE}\ E'_{pH=7.2} = +0.360 V_{SCE} \quad (3)$$

The standard potentials (E^0) for Eqs (1), (2) and (3) were calculated using the following energies of formation: $\Delta G_f^0 Mn^{2+} = -54.5$ kcal/mole, $\Delta G_f^0 \gamma$–MnOOH = –133.3 kcal/mole, and $\Delta G_f^0 \gamma$–MnO_2 = –109.1 kcal/mole. The potentials (E') were calculated at a pH of 7.2 and $[Mn^{2+}] = 10^{-6}$. Dickinson *et al.* (1996) demonstrated that just 6% surface coverage by manganese oxides can increase the resting OCP stainless steels (–200 mV_{SCE}) by some 500mV, which coincides closely with the reported equilibrium potential of the oxides +362mV_{SCE} at a pH of 7.2 (Dickinson *et al.*, 1997; Linhardt, 1998).

Figure 3 shows an XPS spectrum of biofouling deposits on surface of an ennobled 316L SS coupon. The coupon was exposed to pure cultures of *L. discophora* SP-6, and the deposits were analyzed after four minutes argon sputtering. The spectrum shows the presence of manganese.

Our recent results directly correlate the extent and the rate of ennoblement with the rate and amount of manganese oxide deposition on metal surfaces. To determine which environmental factors influence the rate of ennoblement, we exposed 316 L SS coupons at three locations, two creeks and a lake, for 100 days. The open circuit potential (OCP) was monitored periodically, about once a week. The coupons in both creeks reached potential of +350 mV_{SCE} in three weeks. The coupons in the lake reached the final potential of less than

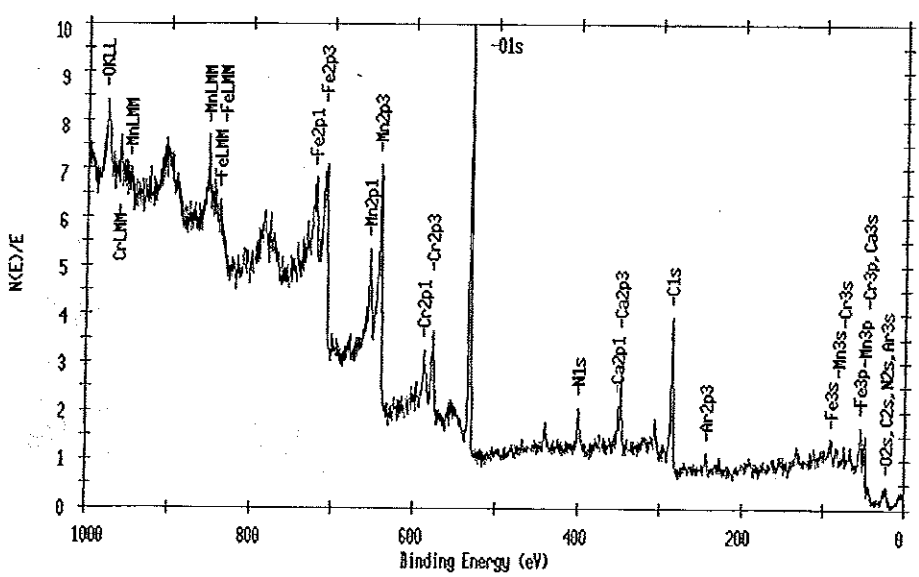
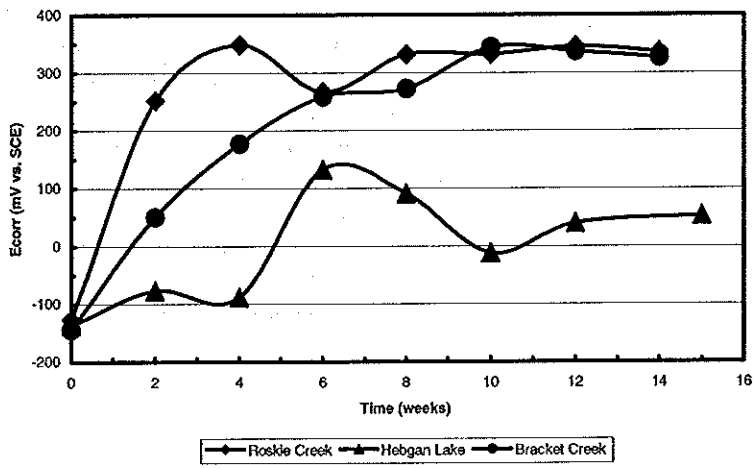


Figure 3 XPS spectrum of biofouling deposits on (ennobled) 316 L SS coupon by *L. discophora* SP-6

+100 mV_{SCE} and the ennoblement rate was very slow. Manganese oxides were deposited on all metal coupons, and their amount roughly correlated with the rate of ennoblement (Figure 4).

Consequences of ennoblement for material performance

Based on several studies conducted in our laboratory we have suggested (Dickinson *et al.*, 1996; Dickinson and Lewandowski, 1996; Dickinson *et al.*, 1997; Olesen *et al.*, 1998; Olesen *et al.*, 2000a,b; Shi *et al.*, 2002) that biomineralized manganese oxides are involved in corrosion of stainless steels. The mechanism in Figure 6 shows the divalent manganese, Mn^{2+} (aq) biomineralized to manganese dioxide, MnO_2(s), with MnOOH(s) being an intermediate product. Both reactions, the oxidation of Mn^{2+}(aq) and the oxidation of MnOOH(s), contribute to the increase in the OCP because both oxides are in electrical contact with the surface and their potential is determined by the concentration of dissolved manganese. Manganese oxides deposited on the surface are reduced to divalent manganese by electrons released at the anodic sites. However, reducing the deposited manganese oxides does not interrupt the corrosion process because the product, divalent manganese ions, are liberated within the manganese oxidizing biofilm, and are reoxidized by the manganese oxidizing microorganisms. This sequence of events, oxidation–reduction–oxidation of manganese, produces renewable cathodic reactants – manganese



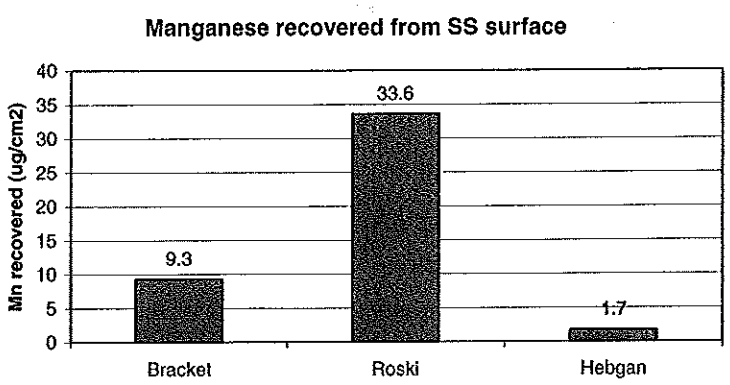


Figure 4 316 L stainless steel coupons exposed to fresh water at three locations in Montana for four months. The rate and extent of ennoblement roughly correlates with the amount of biomineralized manganese recovered from the surfaces after four months (Braughton *et al.*, 2001)

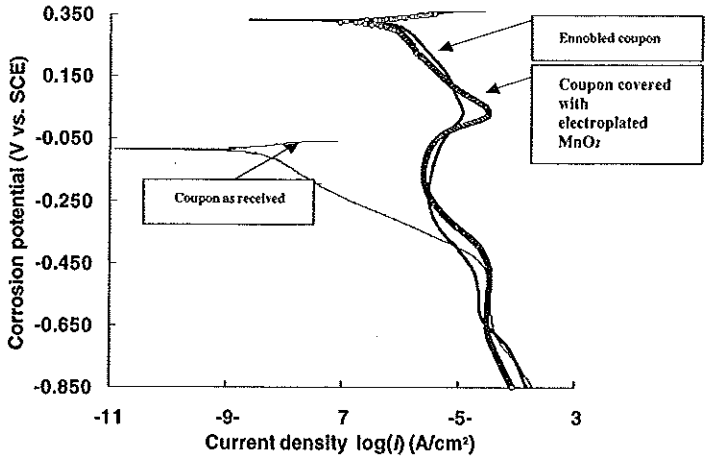


Figure 5 Potentiodynamic polarization curves (316L SS, 0.01M Na_2SO_4, pH 8.30; scan rate: 0.167 mV/s) show typical behavior of non-ennobled, fully ennobled, and MnO_2-plated stainless steel coupons. Both the microbial ennoblement and electroplating of MnO_2 on the metal surface shift corrosion potentials by approximately 300 mV in the noble direction and cause a corresponding increase in cathodic current density at modest overpotentials (around −100 mV)

oxyhydroxide and manganese dioxide. We have partially verified the mechanism in Figure 6 by demonstrating, under well defined laboratory conditions, that 316L stainless steel exposed to manganese-oxidizing bacteria, *L. discophora* SP-6, in a mineral–salt–pyruvate–vitamin medium containing Mn^{2+} exhibited electrochemical characteristics almost identical to the corrosion coupons ennobled in natural waters. Chemical composition of the manganese oxides collected from these coupons was consisted with the mechanism in Figure 6.

Our recent observations suggest that MOB may be directly involved in pit initiation, in addition to the indirect effects caused by the biomineralized manganese oxides. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) images (Figure 7) show micropits formed on 316L SS ennobled by *L. discophora* SP-6. The agglomerates of bacteria encased in sheaths (Figure 7, left) have similar shapes as the pits on the surface of the metal (Figure 7, right). This may indicate that the pits are initiated at sites of bacterial attachment, and then propagate because of the presence of manganese oxides driving the potential in noble direction. To quantify the shapes of the microbes and of the pits, we calculated for each of them their aspect ratios, i.e. the length divided by the width. Fifteen pits initiated by anodic polarization had an aspect ratio of 1.28 ± 0.27, meaning they were

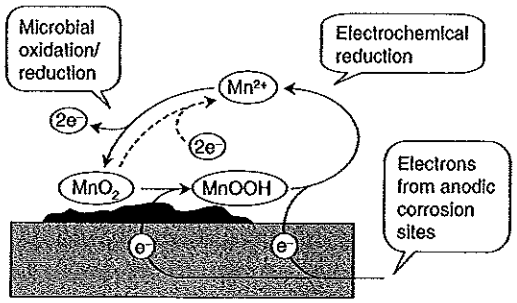


Figure 6 Redox cycling on metal surfaces: hypothetical mechanism of microbial involvement in corrosion of stainless steels and other passive metals (Olesen *et al.*, 2000a)

almost round. In contrast, 71 pits found on coupons ennobled by *L. discophora* SP-6 had an aspect ratio of 9.97 ± 5.50. Also, 20 groups of bacteria we measured had an aspect ratio of 10.0 ± 3.7. Both the bacteria and the pits created in the presence of them were ten times longer then they were wide. These similarities seem to be consistent with our thesis that pits are initiated by the microbes and then propagate because of the high potential established by the manganese oxides.

Conclusions

Manganese-oxidizing microorganisms modify the electrochemistry of passive metals by depositing manganese oxides. These oxides are reduced to divalent manganese by the electrons liberated as result of anodic dissolution of the metal. Manganese ions, the product of the cathodic reaction, are liberated within the manganese oxidizing biofilms, and are reoxidized to manganese dioxide. This mechanism of corrosion relies on redox cycling of manganese on the metal surface, which generates recyclable cathodic reactants, manganese oxides.

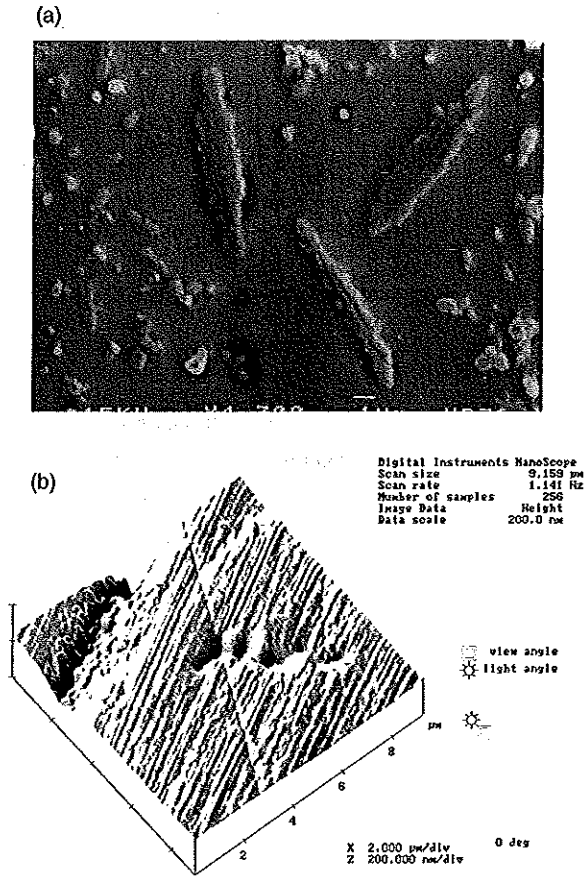


Figure 7 (a) SEM of manganese oxidizing bacteria *L. discophora* SP-6 growing on 316 L SS surface. The image shows groups of bacteria encased in sheaths about 10 µm long. (b) AFM of an indentation in the passive layer generated when the surface was colonized by *L. discophora* SP-6 and then exposed to 0.2 M NaCl to initiate pitting. We commonly find such indentations in the passive layer when the metal was colonized by *L. discophora* SP-6. The size and the shape of the indentations closely resemble the size and the shape of the microorganisms colonizing the surface. Therefore we hypothesize that the pits are initiated at sites of microbial attachment. The line on the left is a mark made to identify the position of the site (Geiser *et al.*, 2001).

The model in Figure 6 shows a sequence of microbial and electrochemical processes that lead to ennoblement and the redox cycling of manganese that can modify corrosion rates. However, the model refers only to thermodynamics; we know very little of the kinetic aspects of the ennoblement. Consequently, we study the effects of such factors as the dissolved manganese concentration, the rate of manganese oxides accumulation, the amount of accumulated oxides, organic carbon concentration, dissolved oxygen concentration, hydrodynamics, temperature, and pH on the rate and extent of ennoblement in lakes and rivers. Although much of the mechanism in Figure 6 remains hypothetical, some of the pathways have been verified experimentally by detecting the intermediate products predicted by the proposed reactions.

Biofilms on metal surfaces modify rates and mechanisms of the surface reactions, thereby influencing the electrochemical processes, including corrosion. By the same mechanism, biofilms mediate the surface reactions and determine rates of many natural and engineered processes, e.g. biomineralization, microbially influenced corrosion of metals, biomining, and bioremediation. Our knowledge of the nature of these modifications is often limited because they are complex, and because we lack suitable experimental and mathematical models to study them. Biofilms on stainless steels constitute an ideal system to study microbe-metal interactions, since the redox reactions involving biofilm and stainless steel are relatively slow, and can be monitored in real time.

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References

Braughton, K., Lafond, R.L. and Lewandowski, Z. (2001). The influence of environmental factors on the rate and extent of stainless steel ennoblement by manganese oxidizing biofilms. *Biofouling* **17** 241–251.

Chandrasekaran, P. and Dexter, S.C. (1993). *Proceedings of Corrosion 1993*, Paper No. 493, Houston, Texas, NACE.

Dexter, S.C. and Gao, G.Y. (1988). Effect of seawater biofilms on corrosion potential and oxygen reduction of stainless steel. *Corrosion*, **44**, 717–723.

Dickinson, W.H. and Lewandowski, Z. (1996). Manganese biofouling and the corrosion behavior of stainless steel. *Biofouling*, **10**, 79–93.

Dickinson, W.H., Caccavo, F. Jr. and Lewandowski, Z. (1996). The ennoblement of stainless steel by manganic oxide biofouling. *Corrosion Sci.*, **38**, 1407–1422.

Dickinson, W.H., Caccavo, F. Jr., Olesen, B.H. and Lewandowski, Z. (1997). Ennoblement of stainless steel by the manganese-depositing bacterium *Leptothrix discophora*. *Applied and Environmental Microbiology*, **63**, 2502–2506.

Eashwar, M. and Maruthamuthu, S. (1995). Mechanism of biologically produced ennoblement-ecological perspectives and a hypothetical model. *Biofouling*, **8**, 203–213.

Geiser, M., Avci, R. and Lewandowski, Z. (2001). Pit initiation on 316 L stainless steel in the presence of bacteria *Leptothrix discophora*. *Corrosion 2001*, Paper 1257, March, Houston, Texas, NACE.

Linhardt, P. (1994). Manganese oxidizing bacteria and pitting of turbine components made of CrNi steel in a hydroelectric power plant. *Werkst. Korros*, **45**, 79–83.

Linhardt, P. (1996). Failure of chromium-nickel steel in a hydroelectric power plant by manganese-oxidizing bacteria. In: Heitz, E., Flemming, H.-C. and Sand, W. (eds), *Microbially Influenced Corrosion of Materials*, Springer Berlin Heidelberg, pp. 221–230.

Linhardt, P. (1998). Electrochemical identification of higher oxides of manganese in corrosion relevant deposits formed by microorganisms. *Materials Science Forum*, **289–292**, 1267–1274.

Little, B., Wagner, P. and Mansfeld, F. (1991). Microbiologically influenced corrosion of metals and alloys. *Int. Mat. Rev.*, **36**, 253–271.

Mattila, K., Carpen, L., Hakkarainen, T. and Salkinoja-Salonen, M.S. (1997). Biofilm development during ennoblement of stainless steel in Baltic Sea water: a microscopic study. *Int. Biodet. Biodeg.*, **40**, 1–10.

Mollic, A. and Trevis, A. (1976). Correlation Entre La Formation de la Pellicule Primaire et la Modification de la Cathodique sur des Aciers Inoxydables Experimentes en eau de Mer aux Vitesse de 0,3 A 5,2 m/s, in: *Proceedings of Fourth International Congress Marine Corrosion and Fouling*, Juan-Les-Pins, Antibes, France.

Olesen, B.H., Avci, R. and Lewandowski, Z. (1998). Ennoblement of stainless steel studied by X-ray photoelectron spectroscopy. *Corrosion 1998*. Paper No. 275, NACE.

Olesen, B.H., Avci, R. and Lewandowski, Z. (2000a). Manganese dioxide as a potential cathodic reactant in corrosion of stainless steels. *Corrosion Sci.*, **42**, 211–227.

Olesen, B.H., Nielsen, P.H. and Lewandowski, Z. (2000b). Effect of biomineralized manganese on the corrosion of behavior of C1008 mild steel. *Corrosion*, **56**, 80–89.

Shi, X., Avci, R. and Lewandowski, Z. (2002). Electrochemistry of passive metals modified by manganese oxides deposited by *Leptothrix discophora*: two-step model verified by ToF-SIMS. *Corrosion Sci.*, **44** 1027–1045

Sedrix, A.J. (1996). *Corrosion of stainless steels*. John Wiley and Sons, Inc. p. 106.

Scotto, V. and Di Marcenaro, G. (1985). The influence of marine areobic microbial film on stainless-steel corrosion behavior. *Corrosion Sci.*, **25**, 185–192.