Effect of biomineralized manganese on pitting corrosion of type 304L stainless steel

Einfluss von biomineralischem Mangan auf die Lochkorrosion von nichtrostendem Stahl des Typ 304L

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During the past few years, biomineralized manganese has been shown to cause ennoblement of various stainless steels to open circuit potentials of 300–400 mV/SCE. We have demonstrated that ennoblement, caused by biologically deposited manganese minerals, along with a relatively low stainless steel pitting potential, caused by the presence of chloride, is sufficient to initiate and drive active pitting corrosion. Stainless steel samples (type 304L), chemically or microbiologically ennobled with manganese dioxide, were exposed to a 0.35% w/v NaCl solution; an environment otherwise not corrosive against the 304L stainless steel. In the first case, steel samples were ennobled by electroplating the sample with a thin film of manganese dioxide, except for a small anodic area. In the latter case, the manganese dioxide was deposited on the steel within biofilms of the manganese oxidizing bacterium Leptothrix discophora SP-6. After 24 h exposure to the chloride solution the samples were investigated by atomic force microscopy (AFM). Both types of ennobled samples were found severely pitted, whereas reference samples (w/o manganese minerals) had remained intact.

In den letzten Jahren hat es sich gezeigt, dass biomineralisiertes Mangan die Veredelung von nichtrostendem Stahl zu freien Korrosionspotentialen von 300–400 mV/SCE verursachen kann. Wir haben gezeigt, dass die Veredelung von nichtrostendem Stahl durch mikrobiologisch gebildete Manganminerale kombiniert mit einem relativ niedrigen Lochkorrosionspotential des nichtrostenden Stahls in chloridhaltigem Wasser hinreichend ist, um aktive Lochkorrosion zu initiieren. Proben von nichtrostendem Stahl (Typ 304L), chemisch oder mikrobiologisch veredelt mit Manganoxid, wurden einer 0,35% w/v NaCl-Lösung ausgesetzt; ein Milieu, das normalerweise bei 304L nichtrostendem Stahl keine Korrosion herbeiführen kann. In dem ersten Experiment wurden die Stahlproben mit Ausnahme von einem kleinen anodischem Bereich mit einem dünnen Manganoxidfilm veredelt. In dem zweiten Experiment wurde das Manganoxid in Biofilmen, bestehend aus dem Mangan-oxidierenden Bakterium Leptothrix discophora SP-6, auf dem Stahl abgelagert. Nach 24 h in der Chloridlösung wurden die Proben mit Rasterkraftmikroskopie (AFM) untersucht. Bei beiden Typen von Veredelung wurden wesentliche Lochkorrosionsangriffe gefunden, gleichzeitig waren Kontrollproben (ohne Manganminerale) intakt.

1 Introduction

The area of Microbiologically Influenced Corrosion (MIC) that involves pitting of stainless steels is generally associated with the activity of sulfate reducing bacteria (SRB) [1, 2]. The influence of SRB on corrosion processes has been extensively studied during the past decades revealing a great deal about their activity [3, 4]. There are, however, other areas of MIC that can be important in relation to stainless steel pitting. Recently, the field of MIC was expanded to reflect an increasing general interest in biomineralization [5]. Particularly the effect of microbially deposited manganese minerals on the electrochemical behavior of metals is being targeted by current studies [6–11]. Though still poorly understood, manganese biomineralization is a common phenomenon in natural waters as well as in industrial systems and water distribution system, where the manganese minerals often are found as black/brownish deposits [12, 13]. Until recently, problems regarding manganese mineral fouling were mostly owed to unwanted coloration of water, particularly drinking water, through manganese biofouling and sloughing within the drinking water distribution system. However new discoveries shows that manganese dioxide (MnO_2), and maybe other manganese minerals too, if deposited on passive metals changes the electrochemical properties of the metal by increasing the open circuit potential (OCP), known as ennoblement [14–18]. Potential ennoblement of passive metals, particularly in marine environments, has been and is still frequently observed and studied [19–22]. Consequently, there exist numerous theoretical explanations to the ennoblement behavior. Deposition of biomineralized manganese, however, is one of the firsts to have a documented effect on the OCP of metals.

During studies of potential ennoblement of 316L stainless steel in a fresh water environment, a connection between biological deposition of manganese oxides on the surface and the

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Table 1. Elemental composition (w/w%) of 304L stainless steel as provided by J&L Specialty Steel, Inc.

Tabelle 1. Chemische Zusammensetzung (Gew.-%) des nichtrostenden Stahles vom Typ 304L im Anlieferungszustand

Fe	Cr	Ni	Mn	Si	Cu	Mo	P	C	S
Bal.	18.27	9.44	1.39	0.54	0.47	0.10	0.022	0.02	0.015

OCP of the steel was discovered [14, 16, 17]. Furthermore it was shown, that the presence of biomineralized manganese oxides solely caused ennobled potentials of the steel in the range of 350–400 mV_{SCE}. Similar effects were obtained by partially covering the steel surface with chemically prepared hydrous MnO_2 [14, 16]. The organic materials constituting the biofilm did not itself cause any changes in the electrochemical properties of the metal.

Investigations of severe pitting failure of CrNi134 steel runner blades in a Dutch hydroelectric power plant, revealed large amounts of manganese rich minerals within corrosion products and biofilms on the surface [15, 18]. Analysis of the mineral deposit revealed a mixture of MnO_2 and MnOOH. OCP of isolated deposit was measured as 570 mV_{SCE} at pH 7.5, 20 °C, and 0.1 mg/L Mn^{2+}. Similar mixtures have been identified in later electrochemical studies of manganese rich corrosion products [23].

In another case elevated amounts of manganese minerals were found at sites of pitting corrosion in a pipeline transferring cooling water from the river Rhine, Germany [24]. The corrosion attacks were, as often reported in cases of MIC, located around welds. Based on these findings the importance of manganese minerals and manganese depositing bacteria among other influences on stainless steel failure was discussed [25].

Another paper reported pitting corrosion of type 304 stainless steel in a potable water treatment plant nine months after startup [26]. The corrosion was most probably influenced by microbiological activity. A number of metal-oxidizing bacterial strains were isolated from black/brown deposits around the corrosion sites. Furthermore the well water contained high amounts of manganese and, following treatment, low concentrations of chlorine. The incident was concluded to be a combined effect of the high concentration of manganese, the deposition of manganese minerals, and the low concentration of chlorine.

Studies of the electrochemical properties of manganese minerals on 316L stainless steel showed that MnO_2 at neutral pH is reduced to divalent manganese through manganese oxyhydroxide [8, 11]. Under those conditions the MnOOH was not stable and there were no net accumulation of this compound at the steel surface. At low pH there were no intermediate products and at high pH only insoluble manganese compounds were thermodynamically stable. It was also shown that at least one strain of manganese oxidizing bacteria, Leptothrix discophora SP-6, mainly deposits manganese as MnO_2. The cathodic activity of MnO_2, through reduction to divalent manganese, was proposed to increase the probability of active pitting and to increase the corrosion rate of active pits [11]. It has previously been stated that the elevated potentials of manganese ennobled stainless steel could reach the pitting potential of the steel [14–18], which in the presence of high amounts of chloride can be as low as zero mV_{SCE}.

This paper addresses the question: “Can the presence of biomineralized MnO_2 on the surface of stainless steel initiate pitting corrosion in a chlorinated environment otherwise resistive to pitting?” Initially the pitting potential of the chosen steel type was determined in different concentrations of chloride, and compared to OCPs of MnO_2 ennobled samples of the same steel type. Secondly, a chloride concentration, which gave pitting potentials below the potentials of ennobled samples, was chosen. Ennobled samples were then exposed to solutions of this concentration, and the surfaces were examined for localized corrosive attacks.

2 Materials and methods

Type 304L stainless steel coupons (∅ 16.8 mm) were punched from 16 gauge sheet metal. The elemental composition of the steel as provided by the vendor, J&L Specialty Steel, Inc., is shown in Table 1.

Coupons were epoxy embedded in polycarbonate rings (height 3 mm, OD 19.1 mm, ID 16.8/10.0 mm) using a slow hardening epoxy (Buehler Epoxide). Fig. 1 illustrates a mounted steel coupon. Copper wires were positioned through 1 mm holes in the sides of the polycarbonate rings and glued to the backsides of the coupons, using a conductive glue (Nickel Print, GC Electronics). The backsides of the rings were filled with the slow hardening epoxy to secure and insulate the electrical connection. Each application of epoxy/glue was allowed 24 h to harden. The mounted coupons were polished first on a series of sandpaper’s ranging from 120 to 600 grit then on polishing mats with 5.0, 0.3, and 0.05 micron aluminum powder. Preparing the samples this way enabled the use of various surface analysis techniques without removing the sample from the holder. These coupons, without further processing, are referred to as type I samples.

Electrochemical experiments were conducted using a potentiostat/galvanostat (EG&G Princeton Applied Research, model 273A) with a platinum mesh auxiliary electrode (30 cm^2 surface area) and a saturated calomel electrode (SCE) as reference. OCPs were measured versus the SCE reference electrode using a handheld multi meter (Wavetek DM23XT, internal resistance 10 mΩ).

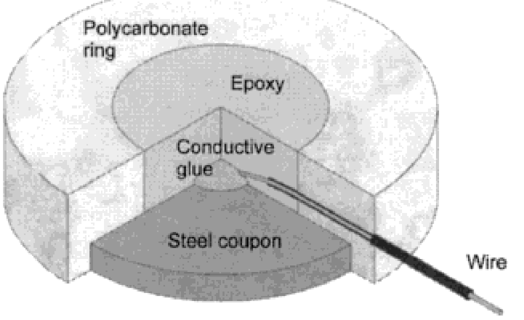

Fig. 1. Illustration of an embedded steel coupon. Only the down facing side of the coupon was exposed

Abb. 1. Darstellung eines eingebetteten Stahlkoupons. Nur die nach unten zeigende Seite des Koupons war dem Medium ausgesetzt

Pitting potentials of the 304L steel (type I samples) were obtained through potentiodynamic polarization. Scans were initiated 50 mV below the OCP and scanned, using a scan rate of 5 mV/sec, to 1.2 V_{SCE} or 1 mA, whichever was reached first. Experiments were conducted at room temperature in 0.1 M Na_2SO_4 solutions with 0, 0.0035, 0.035, 0.35, and 3.5% w/v NaCl.

A number of samples (type I) were electro plated with a thin film of MnO_2 as described previously [8, 11]. Briefly, samples were immersed in an aqueous electrolyte containing 0.1 M Na_2SO_4 and 5 mM $MnSO_4$ at pH 6.5. A total of 30 mC/cm^2 was transferred per sample at a rate of 2 µA/cm^2 corresponding to 13.5 µg/cm^2 or a 270 nm thick film of solid MnO_2. Prior to electroplating, a small drop of immersion oil (a few hundred microns in diameter) was placed in the center of the coupon. The oil drop served as an insulator preventing plating of the underlying steel. Following plating, the oil drop was removed with acetone, having no effect on the composition of the mineral film or the potential of the ennobled coupons. Following plating, the samples were allowed at least one hour to equilibrate in 0.1 M Na_2SO_4. These samples had a large cathodic area covered with MnO_2 and a small anodic area with bare steel. The cathode to anode ratio was about 50 000:1. The composition of the deposited mineral was analyzed by XPS, as described elsewhere [11], revealing only MnO_2. Electroplated coupons are referred to as type II samples. Type I samples served as reference for the type II samples.

Other steel samples (type I) were fouled with a biofilm of the manganese oxidizing bacterium Leptothrix discophora SP-6, within which manganese minerals were deposited onto the steel surface. Cultures of Leptothrix discophora SP-6[27] obtained from American Type Culture Collection (ATCC no. 51168) were grown in sterile mineral-salt-pyruvate-vitamin (MSPV) medium (ATCC no. 1917). Subcultures were preserved by freezing at − 70 °C [28]. Prior to each experiment a frozen culture was thawed and incubated for 48 h in 100 ml MSPV medium. Five ml of this culture was used to inoculate the experimental reactor. The construction and operation of the experimental reactor has been described elsewhere [29]. Briefly a reactor with eight type I steel samples suspended from the lid was filled with 500 ml MSPV containing 200 µM Mn^{2+} as $MnSO_4$, inoculated and run in batch mode for 48 h. Hereafter, the reactor was feed continuously for up to two weeks (1 h retention time) with similar, but five times concentrated, medium and filter sterilized dilution water in a 1:5 ratio. A Saturated Calomel Electrode (SCE), connected to the media through a 1% agar salt bridge containing 1 mM Na_2SO_4, enabled OCP measurements of the steel samples. Biofouled samples prepared this way are referred to as type III samples. As a reference for the type III samples, similar coupons were prepared without added manganese in the growth media. These samples, fouled with a biofilm containing no manganese, are referred to as type IV samples.

Samples of all four types (eight of each type – bare, electroplated, biofouled with Mn, and biofouled without Mn) were exposed to 0.1 M Na_2SO_4 containing 0.35% w/v NaCl for 24 h. During the exposure, the OCP of every sample was measured hourly versus the SCE.

Topographical imaging of selected samples was conducted using contact mode Atomic Force Microscopy (AFM) analyzing an area of until 80 × 80 µm. Prior to exposure, type II samples were mapped within the anodic areas, whereas the type I samples were mapped at randomly chosen sites. Type III and IV samples were mapped as type I prior to fouling. Similar analyses were performed after exposure, searching for changes in the surface topography caused by corrosion attacks. Images were collected at corrosion sites, revealing the depth, width and shape of the attack. Except for light polishing streaks, no unusual topography was found prior to the exposure to chloride.

3 Results

Polarization curves obtained for 304L stainless steel in 0.1M Na_2SO_4 solutions with 0, 0.0035, 0.035, 0.35, and 3.5% w/v NaCl are shown in Fig. 2. In both the reference case, without NaCl, and the case with 0.0035% NaCl, the pitting potential was not reached within the stability of water. In 0.035% NaCl the pitting potential was poorly defined between 500 and 700 mV_{SCE}. The polarization curves showed several peaks of metastable pitting and repassivation in that potential range and the significant current increase could have been caused by decomposition of water. In 0.35% NaCl the pitting potential, at the point where the current rapidly increased, was more precisely determined to be + 300 ± 50 mV_{SCE}. Few of these curves showed repassivation peaks. Curves obtained in 3.5% NaCl, corresponding to a general seawater level, were flattened with a higher overall current and a poorly defined pitting potential around 0 mV_{SCE}. This could have been an indication that at least metastable pitting already happened at OCP.

The OCP of stainless steel samples, ennobled by electroplating with MnO_2, was initially between 550 and 650 mV_{SCE}, but stabilized at + 500 ± 25 mV_{SCE} within one hour in 0.1 M Na_2SO_4. The values correspond well with previously published potential data for MnO_2 plated stainless steel [8, 11]. Anodic areas ranged in size from 20 – 100 µm in diameter. Fig. 3 shows an AFM topographical image of an anodic spot on a type II sample.

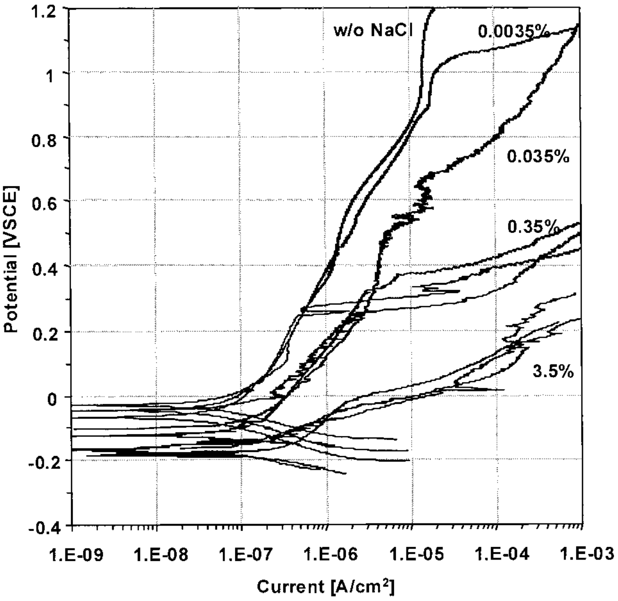

Fig. 2. Polarization curves for 304L stainless steel in 0.1 M Na_2SO_4 solutions with 0, 0.0035, 0.035, 0.35, and 3.5% w/v NaCl

Abb. 2. Polarisationskurven des nichtrostenden Stahles 304L in 0.1 M Na_2SO_4 Lösungen mit 0, 0.0035, 0.035, 0.35 und 3.5% w/v NaCl

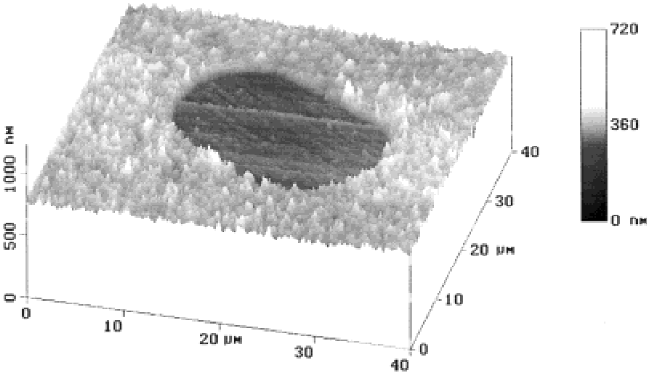

Fig. 3. AFM topographical image of an anodic hole in the cathodic MnO_2 film on an electroplated steel sample

Abb. 3. AFM-Topographiebild eines anodischen Loches im kathodischen MnO_2-Film auf der elektroplattierten Stahlprobe

Samples ennobled through manganese biofouling with L. discophora SP-6, reached stable OCPs of 390 ± 20 mV_{SCE} within one week following inoculation. The potentials remained stable for an additional week until the experiment was terminated.

Based on the OCPs of ennobled samples, a NaCl concentration of 0.35% was chosen for exposure of the ennobled samples. At 0.35% NaCl the pitting potential was about 300 mV_{SCE} and OCP of the ennobled samples were around 400 and 500 mV_{SCE} for biofouled and plated samples respectively. The combination of this concentration and either of the ennobled samples could theoretically lead to active pitting corrosion.

Steel coupons of type I, II, III, and IV were exposed to the 0.35% NaCl solution for 24 h. Biofilms and corrosion products were removed from the coupons by sonication in distilled water for 2 min followed by drying in nitrogen gas. OCPs, collected during exposure to the NaCl solution, were stable between − 200 and − 100 mV_{SCE} for the reference (type I and IV) samples. The potential for the ennobled (type II and III) samples remained initially at 300–500 mV_{SCE}, but dropped after 1–3 h of exposure to values similar to the references.

Reflected light microscopy (100 ×) revealed spots of discoloration on the type II and III samples, whereas the type I and IV samples seemed unaffected. Contact mode AFM showed a large single pit within the anodic areas on the type II samples, and small pits located at cracks in the mineral film within the cathodic area. Fig. 4 shows an AFM topographical image of a pit within the anodic area of a type II sample. After the 24 h exposure, there were still films of manganese minerals covering the cathodic areas. The thickness of the film, however, was reduced compared to the originally plated film (Fig. 3). Pits on the type II samples ranged from 5–15 µm in diameter and 0.5–5 µm in depth. In two cases, the pit depth exceeded the 6 µm limit of the AFM apparatus. No pits were found on the type I samples. In a single case, however, a crevice between the steel coupon and the polycarbonate holder had initiated corrosion. Images of type III samples showed randomly distributed clusters of smaller irregular pits. Fig. 5 shows a top view and a cross section of such a cluster. Few of the pits on these samples exceeded 1 µm in depth. The majority of pits were 0–0.5 µm deep and a few microns in diameter. Type IV samples (the biofouled samples without manganese minerals) showed no sign of corrosion.

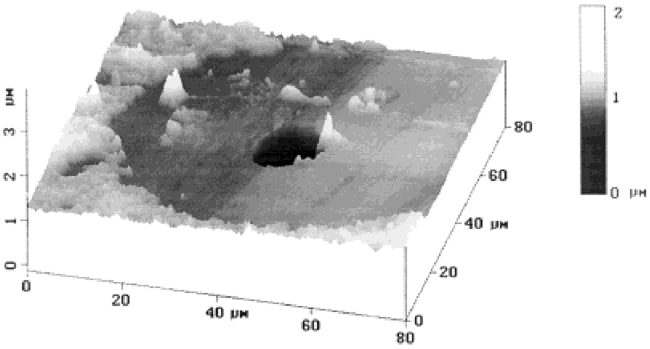

Fig. 4. AFM topographical image of a pit in the anodic area of a MnO_2 electroplated steel sample

Abb. 4. AFM-Topographiebild eines Loches in dem anodischen Bereich einer mit MnO_2 elektroplattierten Stahlprobe

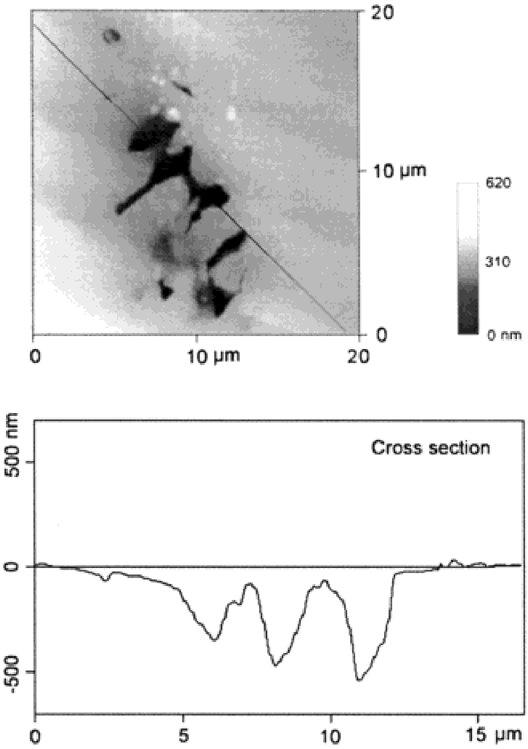

Fig. 5. AFM topographical image and cross section of a group of pits from a MnO_2 biofouled steel sample

Abb. 5. AFM-Topographiebild und Querschliff einer Gruppe von Löcher von einer mit MnO_2 bedeckten Stahlprobe

4 Discussion

From a comparison between the behavior of the references and the ennobled samples, when exposed to chloride, it is clear that the deposited MnO_2 mineral lead directly to pitting corrosion of both types of ennobled samples. These findings prove, at least for 304L stainless steel, our previous hypothesis [11], that the cathodic activity of MnO_2 is sufficient to initiate pitting of stainless steels in a chlorinated environment. Pre-

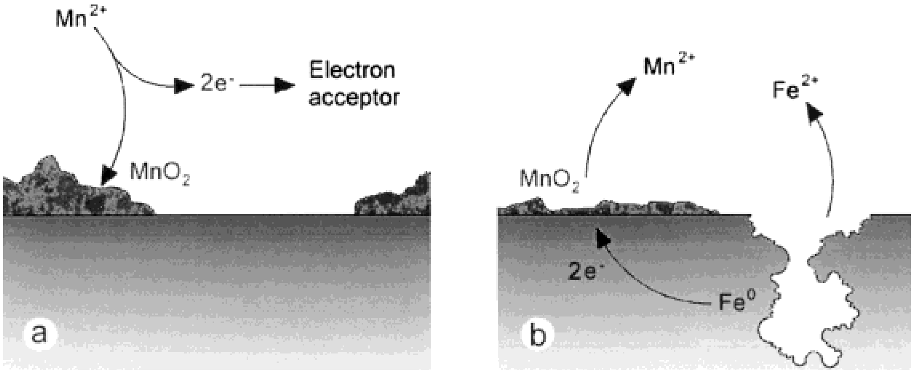

Fig. 6. Schematic illustration of a) the microbial oxidation and deposition of MnO_2 and b) the cathodic reduction of MnO_2 in a corrosion process

Abb. 6. Schematische Darstellung einer a) mikrobiellen Oxidation und Ablagerung von MnO_2 und b) der kathodischen Reduktion von MnO_2 in einem Korrosionsprozess

vious observations [9, 18, 26] of severe pitting corrosion at sites with low chloride concentrations but large amounts of manganese rich minerals corresponds to this behavior.

The onset of pitting corrosion of otherwise passive metals usually results in a sudden drop in the OCP. Our OCP measurements, though not continuous, showed such a drop during exposure of the ennobled samples. Elsewhere published results [9] on the effect of manganese ennoblement on pitting have shown that OCP of ennobled samples dropped when chloride was added. As this behavior was taken as a sign of pitting corrosion, it agrees well with our findings.

It has been stated before [29] that in order to have any effect on the electrochemical behavior of the underlying metal, the manganese minerals have to be in direct electrical contact with the metal. This is one of the basic differences between the two types of ennobled samples. We have previously documented that the electrochemical reduction of manganese dioxide on a metal surface takes place at the mineral/water interface [11, 29]. The type II samples were electrochemically plated with a solid film of manganese dioxide. Though not perfectly smooth, as seen in Fig. 3, each molecule in the film was in electrical contact with the underlying metal, and thus potentially available for electrochemical reduction. In the case of the microbially ennobled samples, the deposition of minerals took place within a structurally heterogeneous biofilm creating patches or clusters of minerals. It is unlikely that all minerals within a biofilm of tenths or hundreds of microns can be in electrical contact with the substratum, thus only a fraction of these minerals were available for electrochemical reduction. Nevertheless, this fraction has several times been proven sufficient to fully ennoble stainless steel [14–29] and now also to initiate pitting corrosion in the presence of chloride.

Fig. 6 summarizes the basic processes involved in ennoblement and pitting corrosion of stainless steel through deposition of manganese dioxide. A number of microorganisms, including L. discophora, are capable of oxidizing manganese (Mn^{2+}) to insoluble minerals like MnO_2. For L. discophora SP-6 the minerals are mainly deposited in the form of MnO_2 [11]. The microbial oxidation process uses different electron acceptors to place the excess electrons. When deposited on the stainless steel, the MnO_2 changes the chemical potential of the surface. Being far more reactive than the passive layer on the steel, it only takes a few percent coverage to change the overall potential of the steel to that of the MnO_2 [9]. Depending on pH and temperature, the potential-determining redox reaction can be one of the following [11, 29]:

$$MnO_2 + 4H^+ + 2e^- \leftrightarrow Mn^{2+} + 2H_2O \tag{1}$$

$$E_0 = 1.315\ V$$

$$MnO_2 + H^+ + e^- \leftrightarrow MnOOH \tag{2}$$

$$E_0 = 1.189\ V$$

The specific reaction influences the redox potential and thus the overall OCP of the metal, however since the reaction (2) is followed by a further reduction of manganese oxyhydroxide (3) the end product will be the same: divalent manganese.

$$MnOOH + 3H^+ + e^- \leftrightarrow Mn^{2+} + 2H_2O \tag{3}$$

$$E_0 = 1.442\ V$$

It has previously been demonstrated that chloride ions can break the passive film on stainless steel [30, 31]. Depending on the steel type, the potential of the steel, and the temperature, it will take a certain chloride concentration to do so, thus the ennoblement itself increases the risk of pitting initiation. Assuming that the pit has been initiated, iron will be dissolved in the pit, generating two excess electrons for each iron atom within the metal matrix. With no cathodic reaction to remove the electrons from the matrix, the dissolution of iron will soon come to an end, due to the build up of electrons, and the pit will repassivate again. Usually the reduction of oxygen or the production of hydrogen gas (depending on whether the environment is aerobic or not) will supply the cathodic reaction. The rate of iron dissolution will then be determined from the total free energy released through either of the cathodic reactions and the anodic dissolution. We have shown earlier [29] that the free energy released through the reduction of MnO_2 to either MnOOH or Mn^{2+} is far greater, coupled to the dissolution of iron, than the reduction of oxygen or the production of hydrogen gas. Thus, due to the thermodynamic properties of MnO_2, the processes (pictured in Fig. 6) will lead not only to an increased probability of pitting corrosion but also to a higher corrosion rate of active pits.

5 Conclusion

The pitting potential of 304L stainless steel in 0.35% w/v NaCl was found to be $+ 300 \pm 50\ mV_{SCE}$.

OCP of 304L stainless steel samples electroplated with MnO_2 were stable at $500 \pm 25\ mV_{SCE}$. Steel samples fouled with a biofilm of Leptothrix discophora SP-6, depositing MnO_2, stabilized at 390 ± 20 mV_{SCE}.

Combining the low pitting potential in 0.35% w/v NaCl with either of the two types of ennobled steel samples resulted in pitting corrosion of the specimens. Reference samples without manganese minerals, either clean or fouled, did not show any signs of pitting following exposure to the 0.35% NaCl solution.

On electroplated samples, pits were formed within specified anodic areas. At these sites, the steel was not plated, but the potential was raised to 500 ± 25 mV_{SCE} by the surrounding plated cathodic areas. The position of the pits within the anodic areas was closely related to the geometry of the area.

Structural and chemical heterogeneity within the biofilm on the fouled samples created similar anodic and cathodic areas on the steel surface that was responsible for the observed randomly distributed clusters of corrosion pits.

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