Effect of oxygen and biofilms on crevice corrosion of UNS S31803 and UNS N08825 in natural seawater

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ABSTRACT

The effect of oxygen and biofilms on crevice corrosion of UNS S31803 and UNS N08825 in seawater was studied. Passivity breakdown occurred through crevice corrosion in UNS N08825 and through transpassive dissolution in UNS S31803 although both alloys displayed crevice corrosion under potentiodynamic conditions. The most severe crevice corrosion occurred in the absence of oxygen and the presence of a biofilm. Microbial adhesion as investigated by fluorescence microscopy occurred mainly outside the crevice and DNA sequencing revealed a shift in biofilm composition as a function of substratum surface and oxygen pressure.

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1. Introduction

In marine environments it is well known that corrosion resistant alloys may still suffer from localized corrosion. In natural seawater there is an increased risk for localized corrosion due to the presence of microorganisms that form biofilms [1–3]. To ensure the appropriate corrosion resistance required for marine applications, a new generation of alloys such as duplex stainless steels (DSS) and nickel-base alloys have been developed. The increased corrosion resistance of these alloys is provided by the presence of higher concentrations of alloying elements such as chromium, nickel and molybdenum. In oxygen containing environments, these alloys form a passivating film on the surface that protects the alloy from aggressive species such as halides. This protective film has self-healing properties when damaged if oxygen is present. However, under certain conditions aggressive ions such as chlorides may compromise the stability of this passivating film, which sometimes, in combination with increased temperatures, may induce permanent rupture of the protective film and promote localized corrosion in the underlying metal [4]. The exact mechanism of passivity breakdown in chloride environments is not known with certainty, but it seems to implicate a potential-controlled adsorption reaction involving chloride ions and specific sites on the metal surface such as irregularities, discontinuities and uneven deposits (e.g. biofilms, debris) [5].

One of the main concerns with high-resistance alloys in marine environments is crevice corrosion (CC). CC is a form of localized attack that occurs within occluded regions or crevices such as overlapping surfaces, incompletely sealed gasket/metal interfaces, threaded joints, irregular penetrating welds or naturally occurring deposits. In the presence of crevices, localized corrosion initiates more easily owing to the presence of a crevice gap where the electrochemical conditions become different to those on the boldly exposed surface [6]. Hitherto, different models for crevice corrosion initiation have been postulated. Existing theories include the development of a critical crevice solution (CCS) [7], which refers to the formation of a differential aeration cell between the crevice gap and the outer solution followed by a gradual build-up of aggressive species within the crevice electrolyte. An alternative theory advocates the development of a current resistance (IR) drop [8,9] which refers to the electrode-potential variation between the crevice and the outer surface. This theory stipulates that when the IR drop inside the crevice becomes large enough to force the crevice to move to an active potential, passivity is destroyed and active dissolution of the metal occurs. Crevice corrosion initiation has also been linked to metastable pitting that is stabilized at the occluded environment [10,11]. This theory suggests that metastable pits formed within a crevice are more likely to become stabilized due to the resistive barrier of the crevice geometry.

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Sulphide inclusions in the passive film were also proposed to play a role in CC initiation since chemical analysis of the crevice electrolyte during the induction period of CC showed that sulphur species were the dominant compounds [12].

The involvement of microorganisms in marine corrosion has long been recognized [13–16]. Microbial adhesion and the consequent biofilm formation on structural materials in seawater have shown to increase the likelihood of localized corrosion by different means. For instance, ennoblement of passive alloys – a shift of the open circuit potential in the anodic direction due to bacterial presence and/or activity – may reduce the initiation time for pitting and crevice corrosion [17,18]. Mechanisms of biofilm-enhanced corrosion also include cathodic depolarization [19], production of aggressive metabolites [20] and catalytic enzymes [21,22] and bio-deposit formation leading to crevice type of attack [23]. Biofilms have also been shown to decrease initiation times for localized corrosion by lowering the critical pitting and repassivation potential of alloys [2,24]. The role of biofilms in crevice corrosion propagation has also been examined [25]. It was suggested that the increased propagation rate was caused by catalysis of the cathodic reaction by biofilms.

The investigation of biofilm communities on corroding surfaces has become essential to advance the understanding of the complex mechanisms involved in the biofilm-enhanced corrosion processes. The study of biofilm community structure may provide information on the interactions of biofilm populations with different steel grades and physicochemical variables by investigating the shift in biofilm communities in response to environmental conditions. Hitherto, only a few studies have considered analyzing the microbial community structure of biofilms on corroding surfaces [2,26–28] and only one recent study has been conducted to investigate microbial communities in biofilms developed on artificially creviced surfaces [29].

In marine environments, it is of particular importance to investigate the role of oxygen in the kinetics of metal dissolution as it is a critical element not only in the formation and maintenance of passive films in active–passive alloys, but also it is a determining factor in the structure and physiological activities of biofilms on surfaces [30]. In addition, the role of oxygen in crevice corrosion has been previously reported and oxygen depletion appears to be a prerequisite for the initiation and stabilization of crevice corrosion [7]. Therefore, it appears of vital importance to investigate the interactions between crevice corrosion of high-resistance alloys and biofilm formation in natural seawater, and in particular to study the role that oxygen plays on those interactions. Nonetheless, a comprehensive study with focus on these aspects is lacking.

In this study, experiments were designed to sustain biofilm growth on alloys fitted with an artificial crevice assembly in natural seawater in the presence and absence of oxygen for up to 30 days. Experiments were maintained under closed experimental conditions, without water replenishment, in order to simulate the interior of off-shore pressure equipment in which seawater from hydrotesting, ballast or preservation can remain inside the equipment for extended shut-down periods. We investigated crevice corrosion on UNS S31803 DSS and UNS N08825 nickel-base alloy in seawater by conducting corrosion potential (E_{corr}) monitoring, potentiodynamic polarization tests and surface analysis by optical microscopy. In particular we examined the influence of oxygen and marine biofilms on the crevice corrosion initiation and repassivation of the alloys in seawater at 30 °C, a typical temperature for off-shore assets, and a suitable temperature for the growth of biofilms composed of mesophilic microorganisms. Microbial adhesion was studied using 4,6-diamidino-z-phenylidole (DAPI) fluorescent dye and the biofilm community structure was examined using denaturing gradient gel electrophoresis (DGGE) of polymerase chain reaction (PCR) amplified 16S rRNA genes and DNA sequencing to help establish a relationship between biofilm community structure and crevice corrosion associated with the presence or absence of oxygen in seawater.

2. Experimental procedure

2.1. Specimen preparation

Commercial UNS S31803 stainless steel and UNS N08825 nickel–base alloy were used in this study. The chemical composition of these alloys in weight per cent is described in Table 1. Square coupons of approximately 50 cm^2 surface area ($50 \times 50 \times 5$–7 mm thick) were drilled in the centre with a 7 mm diameter hole. For electrochemical testing, an electrical connection was established via a copper wire soldered to one side of the coupon. To prevent crevice corrosion, samples were electrocoated with a protective epoxy (Powercron® 6000CX, PPG Industrial coatings) at the surface area where the spot weld was made for electrical connection and uncovered weld areas were further covered by epoxy resin (Belzona 1391, Belzona polymerics Ltd). The coupon surface area was wet ground up to 600 grit finish (SIC grinding paper), degreased with acetone and dried with nitrogen gas. Artificial crevices were formed using spring loaded crevice assemblies as described elsewhere [31]. A schematic view of the arrangement for crevice evaluation is shown in Fig. 1. Crevice formers (outside diameter 20 mm, inside diameter 7 mm, height 15 mm) were made of PVDF (polyvinylidene diflouride), ground to 1200 grit finish, cleaned and dried before use and four disc springs (nylon coated steel) were used to maintain a constant load corresponding to the 3 Nm applied torque (Fig. 1). Test specimens and all pieces of the crevice assembly were soaked in Decon® 90 (Decon laboratories Limited) for 3 h and sterilized by immersion in 70% ethanol for 1 h before assembling and exposure.

2.2. Test conditions

Artificially creviced coupons were formed and immersed in natural seawater. Spring loaded creviced assemblies were maintained under open-circuit closed experimental conditions (without seawater replenishment) for 30 days to allow a biofilm to develop on the specimens. Seawater was collected from 20 m depth in the Indian Ocean off Rottnest Island (Western Australia). The chemical composition of the seawater is shown in Table 2. To evaluate the effect of oxygen and biofilm formation on crevice corrosion, four reaction vessels were set up for each alloy (Table 3). A schematic of the experimental set-up is shown in Fig. 2. A continuous filter-sterilized (0.22 μm nylon syringe filters) gas (either air or N$_2$) inflow was maintained in all vessels to ensure consistent levels of gas saturation for the duration of the experiment. Dissolved oxygen was monitored using an Orbisphere 3655 oxygen analyser (Hach Company). Test temperature was maintained at 30 °C using a circulating water bath. Coupons were immersed in the electrolyte solution using a Teflon holder placed at the bottom of the cells. Five sample replicates were immersed in each cell which was filled with 7 L of seawater. Control experiments consisted of artificially creviced coupons immersed in filter-sterilized seawater (0.22 μm polycarbonate filters). At the completion of exposure, potentiodynamic polarization tests, surface analyses and biofilm collection from specimens were conducted. Three specimens were used for electrochemical measurements and the remaining two for microbiological analysis.

2.3. Electrochemical measurements

All experiments were conducted using a conventional three electrode cell assembly [32]. A double junction Ag/AgCl electrode