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Interactions between steels and sulphide-producing bacteria—Corrosion of carbon steels and low-alloy steels in natural seawater

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ABSTRACT

Metallic infrastructure immersed in natural seawater is exposed to important corrosion phenomena, which are sometimes characterised by microorganism influenced corrosion. The presence of sulphide-producing bacteria is generally associated with catastrophic cases of material degradation. In this work, commercial steel grades (carbon steels and low-alloy steels) are immersed for approximately 1 year in two types of natural seawater, which contain different concentrations of sulphide-producing bacteria. Gravimetric, microbiological, and electrochemical measurements and corrosion product analyses indicate that in seawater the observed corrosion phenomenon is composed of two different phases. The first phase is characterized by decreased corrosion kinetics correlated with a higher concentration of sessile sulphide-producing bacteria and the formation of sulphur-containing chemical species. The second phase is marked by an increased rate of corrosion. This multidisciplinary study demonstrates the complexity of the interactions between steels and bacteria. The presence of alloying elements in the steel composition affects the rate of corrosion and growth patterns of sessile sulphide-producing bacteria. At the same time, the presence of sulphide-producing bacteria affects in the process of steel corrosion in natural seawater.

1. Introduction

The study of marine corrosion of low-alloy steels began 50 or 60 years ago [1–8], in order to understand the effect of alloying elements on corrosion resistance properties. In these experiments, microbiological parameters were rarely considered. In the 1990s, researchers began to consider the influence of microorganisms, such as bacteria, on marine steel corrosion [9]. Tests were performed under both natural and laboratory conditions [9]. The following kinds of bacteria are implicated in marine corrosion mechanisms and thus receive the most attention: the sulphide-producing bacteria, like sulphate-reducing bacteria (SRB) and thiosulphate-reducing bacteria (TRB) [10,11]. Several theories propose to explain how microorganisms facilitate corrosion, but none of them is comprehensive and clearly explains the effects of microorganisms or of alloying. Von Wolzogen Kuhr et al. have attempted to explain the phenomenon by applying cathodic depolarisation theory [12] and argue that consumption of hydrogen by SRB could accelerate the dissolution of iron at the anode. This theory is highly debated, and instead it seems that sulphide-producing bacteria play a more indirect role in the mechanism of steel corrosion. For instance, their metabolic byproducts may change certain environmental conditions, such as the local pH, the local chemistry or the concentration of sulphur containing chemical species present. These local conditions could be favourable parameters and corrosion mechanisms could colour occur.

Iron sulphides could form a continuous film on the surface of the steel [13] whose thickness and structure could confer protective or adherent properties [14,15]. Ruptures in this film could also lead to a system of enhanced galvanic corrosion.

Based on previous immersion test results [1–6], Melchers proposes a model for the corrosion of low-alloy steels in seawater [16,17]. Only generalised corrosion is considered in this model, which is composed of four successive phases. During the first phase, the rate oxygen diffusion from the medium onto the steel surface is limiting, and linear corrosion is observed. In the second phase, the rate of oxygen diffusion through the corrosion products becomes limiting and results in non-linear corrosion. Thickening of the corrosion product layer lowers the rate of diffusion. In the third phase, anaerobic conditions favour the rapid growth of SRB. The fourth and final phase is a stationary state with respect to both bacterial growth and the corrosion rate. Assuming that the same set of experimental parameters might affect each phase differently, seemingly

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Table 1
Composition and commercial designation of the tested steels

Code	Commercial designation	%C	%Mn	%Si	%P	%S	%Cr	%Mo	%Ni	%Cu
A	XC6	0.050	0.213	<0.010	0.005	0.005	0.009	<0.005	0.017	0.014
B	2C22	0.208	0.680	0.343	0.016	0.030	0.216	0.026	0.194	0.161
K	30CND8+S	0.281	0.665	0.224	0.010	0.054	2.160	0.393	2.110	0.164

contradictory results might be reconciled in accordance with the environmental conditions and duration of immersion.

The objective of the present work is to better understand the involvement of bacteria, especially sulphide-producing bacteria, in the marine corrosion phenomenon. A model consisting of several phases is proposed and discussed.

2. Experimental procedure

2.1. Steel samples

The composition and commercial designation of the steel alloys examined are given in Table 1. Metals A and B are mild steels, and metal K is a low-alloy steel. Samples with dimensions 60 mm × 10 mm × 1 mm are employed. They are placed on a titanium sample holder when immersed in seawater. The sample holder before immersion is shown in Fig. 1.

2.2. Test media

The steel samples are immersed in two different seawater media. The first medium is seawater pumped directly from the Harbour of Flamands (near Cherbourg, France) and is henceforth called “non-treated seawater”. The second medium is the same seawater after it has been subjected to particle filtration and ultraviolet irradiation, and it is henceforth deemed “treated seawater”. This treatment significantly reduces only the concentration of sulphide-producing bacteria present (<10 bacteria ml^{-1} in the treated seawater, >10^3 bacteria ml^{-1} in the non-treated seawater). Other kind of cultivable planktonic bacteria are nearly equivalent in both seawaters: a contamination could occur by aerial bacteria or inadequate sterilisation of the complete experimental set-up.

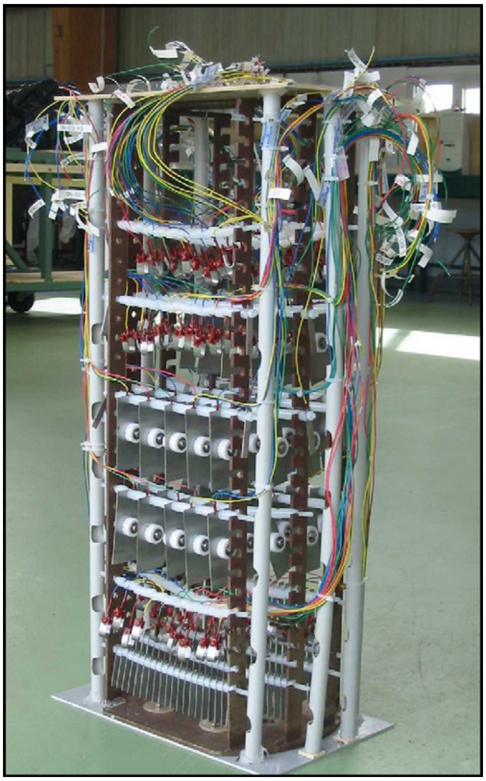

Fig. 1. Titanium holder with metallic samples before immersion.

2.3. Gravimetric measurements

Steel samples are submerged in their respective seawater baths and examined after 2 months, 5 months, 8 months, and 11 months of immersion. An electrochemical technique is used to remove any oxides [18]. This electrochemical technique consists in the imposition of a potential between the sample (related to cathode) and a graphite anode, both electrodes being immersed in a saturated lithium chloride dimethylformamide bath. Oxides are reduced and metallic lithium settles on the sample. Then the sample is rinsed with demineralised water and with ethanol. This procedure could be repeated if necessary after weighing until points of gravimetric measurements are stable in accordance with the NF ISO 8407 standard.

2.4. Microbiological measurements

Planktonic and sessile sulphide-producing bacteria adhering to the steel and its corrosion products are quantified using the technique of the most probable number (M.N.P.) [AFNOR standard, NF T 90-413, Essais des eaux, 1985]. A culture medium based on that outlined by Magot [19] is employed, but seawater is used instead of demineralised water.

Every month, the concentration of planktonic sulphide-producing bacteria is measured and controlled in both the treated and the non-treated seawater samples.

To obtain the sessile sulphide-producing bacteria concentrations, metallic samples are placed in sterile demineralised water and deposits (biofilm and corrosion products) are extracted from the metallic sample using an ultrasonic bath (5 min, power 250 W, frequency 35 kHz). The M.N.P. technique is then applied on this bacterial solution.

2.5. Electrochemical measurements

The following electrochemical measurements are performed monthly on dedicated steel samples of the same dimensions: corrosion potential, polarisation resistance, and impedance. Measurements are made with a Gamry potentiostat and are analysed with Gamry Echem Analyst software. The reference electrode is a saturated calomel electrode, and the titanium sample holder acts as the counter electrode. For polarisation resistance assessment, current is measured as the potential is swept from −10 mV to +10 mV across the corrosion potential. Impedance measurements are also realised with a Gamry potentiostat in the same potential region and consist in five points per decade in the frequency range 10 mHz to 100 kHz. The Gamry Echem Analyst software is used to explore the impedance diagrams. The successive loops observed on the diagrams are fitted with RC equivalent electrical circuits in the adequate frequency range.