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Localized corrosion of carbon steel in marine media: Galvanic coupling and heterogeneity of the corrosion product layer

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ABSTRACT

Corrosion product layers formed on carbon steel coupons after 6–8 years of permanent immersion in natural seawater were characterized by X-ray diffraction and μ-Raman spectroscopy. Some of the coupons showed blisters of corrosion products on a surface covered elsewhere by a much thinner layer. In anodic zones, the formation of the sulfate green rust proved to be favored at the expense of that of magnetite. In contrast, the formation of magnetite was favored in cathodic zones, together with that of aragonite and carbonated corrosion products. The galvanic effects are then self-sustaining via their influence on the corrosion products.

1. Introduction

Localized corrosion phenomena were often observed in marine media, and generally associated with bacterial activity [e.g. 1–8], the heterogeneous nature of the biofilm explaining the non-uniformity of the corrosion process. For vertical steel structures, differential aeration can also lead to the localization of the corrosion process. The immersed part of the structure that is close to the seawater/air interface is more aerated and may thus be a cathodic zone with respect to lower parts of the structure [9–11]. In both cases, the heterogeneity of the medium is the origin of the local nature of the corrosion phenomenon. However, heterogeneities of the carbon steel surface also favor such localized processes. As a consequence, the corrosion process is always somewhat "localized", i.e. not perfectly uniform. This must be kept in mind and for this reason, a corrosion process that does not lead to significantly increased local corrosion rates will be denoted as "uniform" (with inverted commas). Similarly, when the corrosion rate is significantly higher in a specific zone of the metal surface than that observed for the rest of the surface, the process will be denoted as "localized".

It is generally admitted that the corrosion rate is governed by the diffusion of oxygen through the corrosion product layer once this layer inhibits sufficiently the transport of oxygen from seawater to metal surface [12–14]. This inhibition is not likely to occur simultaneously at all regions of the metal surface because differential aeration and biofilm can induce the formation of a heterogeneous corrosion product layer. The term "heterogeneous" means here that the composition, electrical properties and thickness of the layer may not be the same on all parts of the surface. The local formation of electronic conductors such as iron sulfide (FeS), magnetite (Fe_3O_4) or other conductive compounds can for instance favor the formation of cathodic zones [15,16] which may lead to galvanic couplings between different areas of the steel surface. Mechanisms involving FeS as cathode for oxygen reduction were also proposed for corrosion processes influenced by sulfide-producing micro-organisms [17]. More particularly, the conductivity of FeS should play a key role in the corrosion phenomena associated with electroactive sulfate-reducing bacteria because it allows the electrons to go on flowing from the metal to the bacteria [18]. In first approach, it can be considered that anodic and cathodic zones may correspond to de-aerated and aerated areas respectively. Regions are de-aerated when oxygen cannot reached the metal surface because its transport is strongly hindered and/or because it is consumed by reaction with Fe(II)-based compounds and aerobic bacteria. In aerated zones, O_2 may reach the metal surface or be reduced on electronic conductors (magnetite or FeS) connected to

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the metal surface. So de-aerated areas tend to be anodic zones and aerated areas tend to be cathodic zones.

One may wonder whether the heterogeneity of the corrosion product layer can favor the localization of the corrosion, that is can make it worse or make it last longer via a self-sustaining process. For instance, Han et al. [19,20] even proposed a model where the heterogeneity of the corrosion product layer could initiate “localized” corrosion. To address this problem, a detailed study was performed in the frame of the Aduscor research program of the Technological Research Institute Jules Verne of Nantes (France). Various carbon steel coupons of different sizes were immersed vertically in natural seawater at low depth so that differential aeration could play a role and favor “localized” corrosion processes as observed in previous works [9–11]. Some coupons were simply left at open circuit potential (OCP) while others were pretreated before being electrically connected for the study of the galvanic effects induced during immersion in seawater. In this last case, the galvanic current and the mixed potential of the galvanic couple were measured with a zero resistance ammeter (ZRA).

After 6–8 years of immersion, the resulting corrosion product layers were thoroughly characterized by X-ray diffraction (XRD) and Raman micro-spectroscopy. As shown in previous studies [21–23], XRD is not suitable for the detection of the FeS phase forming in seawater. Actually, due to the alkaline conditions, FeS remains in its initial nanocrystalline state [24]. Consequently, Raman spectroscopy, which is in contrast very sensitive to nanocrystalline FeS, was used as a complementary characterization method. Moreover, μ-Raman spectroscopy allows an analysis at a microscale and XRD at a macroscale. Their combined use allows identifying all the solid phases present, determining their location inside the corrosion product layer (via μ-Raman spectroscopy) and quantifying them (via XRD).

2. Experimental

2.1. Materials

The coupons were made of S355 or TU250B carbon steels. The compositions of these materials are given in Table 1. They show that the two steels differ mainly in their carbon, manganese and copper contents. The other elements are found whether in very small amount in both steels (Al, Cr and Ni) or in similar proportions (P, S and Si). Various studies were devoted to the effects of alloying elements on the corrosion rates of low alloy steel in seawater [25–28]. It was generally concluded that C has little or no effect, while Mn and Cu have only a little effect, but still controversial.

The surface of the coupons was shot blasted (Sa 2.5, angular shot), which led to a roughness value of 50–70 μm, degreased with acetone and dried. An electrical connection with a copper wire was achieved by welding and the weld was isolated from seawater by a thick layer of epoxy resin. However, the observations performed after the 6–8 year immersion period demonstrated that the metal was more degraded around the resin-steel interface than anywhere else. This small region of the surface was consequently excluded in each case from the study.

The immersion experiments were performed at the DCNS marine corrosion department in Cherbourg (France). The natural seawater was pumped directly from the English Channel to flow continuously at a rate of 100 L/h through the electrochemical cells before being rejected back to sea. Temperature, oxygen concentration and conductivity were followed over time. Temperature varied between 5 °C in winter and 18 °C in summer. The variations of conductivity followed those of temperature, with a minimum value around 34 mS cm^{-1} in winter and a maximum around 46 mS cm^{-1} in summer. In contrast, oxygen concentration varied oppositely to the temperature from 5 mg L^{-1} in summer to 10 mg L^{-1} in winter. The average composition (main ionic species only) of the pumped sweater was determined at: $[Cl^-] = 19$ g kg^{-1}, $[SO_4^{2-}] = 2.7$ g kg^{-1}, $[HCO_3^-] = 0.14$ g kg^{-1}, $[Na^+] = 10$ g kg^{-1}, $[Mg^{2+}] = 1.3$ g kg^{-1}, $[Ca^{2+}] = 0.41$ g kg^{-1} and $[K^+] = 0.4$ g kg^{-1}.

Three experimental conditions were considered, as summarized in Table 2. First, a small (2.5 cm × 2.5 cm) square coupon, denoted “A”, was left 5.7 years at OCP in the flowing natural seawater. Secondly, a large (10 cm × 10 cm) square coupon (“B”) was left 6 years at OCP in the same conditions. Thirdly, two coupons (“C” and “D”) were coupled 8 years in natural seawater. They were previously treated so as to be covered with different corrosion product layers when connected to each other. Coupon C (5 cm × 5 cm) was covered with a magnetite (Fe_3O_4) layer using the following procedure. First, the sample was oxidized in air at 900 °C, which led to an oxide layer consisting of a thick inner stratum of FeO, an intermediate stratum of Fe_3O_4 and a very thin outer stratum of α-Fe_2O_3 [29]. Secondly, the sample was maintained at 500 °C. FeO is not thermodynamically stable under 570 °C and transforms into a mixture of FeO and Fe_3O_4. Before immersion in seawater and coupling with coupon D, the surface of coupon C was lightly abraded with a SiC paper (grade 600) to remove the outer stratum of α-Fe_2O_3. This coupon was then expected to act as the cathode of the galvanic couple because oxygen reduction could take place on the surface of the magnetite layer.

Coupon D (5 cm × 5 cm) was first painted so that it remained only 1 cm^2 of active metal surface on one of its sides. It was coupled five days with a Ni-based alloy (Inconel 625) in seawater at room temperature so that a magnetite-free corrosion product layer could form on its surface (assuming that a strong anodic polarization favors GR(SO_4^{2-}) and FeOOH, see Section 3.2). It was connected after that to coupon C in another cell. Coupon D was expected to act as anode because oxygen reduction should be hindered by the corrosion product layer, assumed to be only composed of insulating compounds. Electrodes C and D were immersed at the same depth and were kept parallel and separated by the same distance of 5 cm all along the 8 year experiment. The 1 cm^2 of active (unpainted) area of coupon D was facing coupon C.

Electrochemical measurements (galvanic current and mixed potential or OCP) were carried out respectively with a ZRA from ACM instruments and a PHM210 Radiometer millivoltmeter. A saturated calomel electrode (SCE) was used as reference electrode (E = +244 mV/SHE at 20 °C).

2.2. Characterization of the corrosion product layers

The obtained corrosion product layers were analyzed by X-ray diffraction (XRD) and μ-Raman spectroscopy. This analysis requires that the samples are preserved from oxidation by air. For this reason, the coupons removed from seawater were immediately set in carbon ice (−79 °C) before being carried away for analysis (at LaSIE laboratory in La Rochelle, France). The coupons were then immediately transferred into a freezer where they were maintained at −24 °C. This experimental procedure was used in previous works and proved adequate [23,30]. The samples are analyzed in this frozen state so that the corrosion product layers, that contain a lot of water, can be handled easily. A peculiar part of the layer can then be easily removed from the metal surface. Moreover, when its thickness exceeds 2–3 mm, the layer can be split in 2 or 3 strata.

The Raman analysis was performed at room temperature on a Jobin Yvon High Resolution Raman spectrometer (LabRAM HR Evolution) equipped with a confocal microscope, a Peltier-based cooled charge coupled device (CCD) detector and a solid-state diode pumped green laser (532 nm). The laser power was reduced between 25% and 1% of the maximum (i.e. between 1.94 and