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Electrochemical investigations on crevice corrosion of a martensitic stainless steel in a thin-layer cell

Sabrina Marcelin [a], Nadine Pébère [a,*], Sophie Régnier [b]

[a] Université de Toulouse, CIRIMAT, UPS/INPT/CNRS, ENSIACET, 4 Allée Emile Monso – CS 44362, 31030 Toulouse cedex 4, France
[b] Institut Catholique d'Arts et Métiers, 75, Avenue de Grande-Bretagne, 31300 Toulouse, France

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ABSTRACT

This paper focuses on crevice corrosion resistance of a martensitic stainless steel. First, electrochemical measurements were performed in deaerated bulk electrolytes for different chloride concentrations and different values of the pH to determine the critical parameters leading to dissolution or breakdown of the passive film. Then, a thin-layer cell was designed to confine the electrolyte between two parallel stainless steel planes. Impedance measurements obtained for different immersion times and electrolyte thicknesses clearly showed the influence of these two parameters on the crevice corrosion rate. A significant decrease of the corrosion resistance when the medium is increasingly confined was observed. The data obtained in the bulk electrolytes were used to determine the critical conditions in the thin-layer cell which impede the repassivation of the stainless steel (pH and [Cl$^-$]).

1. Introduction

Martensitic stainless steels are mainly used for applications where high mechanical performance is required [1,2]. However, due to their low chromium content, they are relatively sensitive to localized corrosion, particularly crevice corrosion encountered in confined environments. In these areas, oxygen is progressively consumed and cannot be renewed by diffusion or convection. Outside the confined area, the cathodic reaction of oxygen reduction still occurs on the metal surface, whereas, in the confined area, the metal surface becomes the anode. The corrosion processes lead to the modification of the chemical composition of the electrolyte in the crevice with simultaneous acidification and an increase of chloride ion concentration [3–5]. When the pH and the Cl$^-$ concentration in the crevice solution reach critical values, depassivation of the stainless steel with active dissolution occurs. This mechanism is the classical one proposed in the literature for the initiation of crevice corrosion. However, the crevice corrosion mechanisms are complex due to the occurrence of different related phenomena such as ohmic drop inside the crevice [6–8] and formation of metastable pits [9–13]. Zadorozne et al. [14] showed that the ohmic drop was not a necessary condition for crevice corrosion propagation for nickel alloys bearing chromium and molybdenum, but was a consequence of the crevice corrosion process. Abdulsalam [8] showed that crevice corrosion on iron in acetate medium (pH = 4.6) started at a potential difference of 0.4 V between the opening and the bottom of the crevice. In the case of a Ni–Cr–Mo alloy (Alloy-22), which presents a higher corrosion resistance to various forms of localized corrosion, Jakupi et al. [12,13] showed that the kinetics of the cathodic reaction (O_2 reduction) on passive surfaces outside the crevice are a key factor in crevice corrosion propagation. Under open-circuit potential, the crevice corrosion initiated but the propagation was limited by repassivation. This was attributed to the kinetics of O_2 reduction which is too slow to sustain the conditions required for the corrosion propagation within the crevice. To avoid the repassivation of the steel, they applied different currents to the anode. An anodic current density of 250 $\mu A\ cm^{-2}$ appeared to be the minimum required to establish active crevice corrosion (5 M NaCl, 120 °C) [12,13].

Investigation of crevice corrosion requires reproducing artificial crevices. Different setups have been described in the literature. Based on normalized tests, multiple crevice assembly was often used [14–18]. Cai et al. [17] investigated the effects of applied torque and crevice forming materials on the corrosion behaviour of 316L stainless steel. They showed that the corrosion rate increases with an increase of the applied torque. In other works, the electrolyte was confined on the metal surface by using an insulating plane [9,19]. One part of the metal surface, in the confined area, is the anode and another part of the metal surface, in contact with the bulk solution, is the cathode. Na et al. [19] showed, for a ferritic 430 stainless steel, that the initiation time of crevice corrosion

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* Corresponding author. Tel.: +33 5 343 234 23.
E-mail address: nadine.pebere@ensiacet.fr (N. Pébère).

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decreased when the chloride ion concentration increased or when the electrolyte thickness above the stainless steel decreased. Another setup was used where the cathode and the anode were physically separated but electrically connected [9]. Two stainless steel electrodes were used as working electrodes. One was placed in the crevice solution and the other was immersed in the bulk solution. The upper part of the setup was composed of a thin square section PTFE ring. The electrolyte volume in the crevice was limited by the thickness of the PTFE square section ring. A thin-layer cell composed of a Fe–36Ni steel cylinder electrode facing a polymeric cylinder was used by Fiaud et al. [20] to confine the electrolyte. Electrochemical impedance measurements highlighted a radial potential distribution on the steel surface due to the ohmic drop in the cell. Zinc corrosion was also investigated using the same thin-layer cell [21]. The authors showed that when the electrolyte thickness decreased, charge transfer resistance increased. This result was explained by an impoverishment of dissolved oxygen in the confined medium. The major drawback of the different devices mentioned above is the difficulty to accurately control the electrolyte film thickness. Recently, based on the thin-layer cell setup [20,21], an innovative device was developed to minimize the errors of parallelism and to adjust the setting of the electrolyte film thickness (±20 μm) [22]. This setup allows a thin electrolyte layer, down to 80 μm, to be confined between two parallel planes. The electrolyte film geometry can be accurately controlled by using a procedure based on high-frequency impedance measurements on three small platinum electrodes. This setup was used to show the presence of a crevice between copper and aluminium and allowed pH values inside and outside the crevice to be measured [23].

The aim of the present work was to investigate the corrosion behaviour of a martensitic stainless steel (SS) in confined medium and in crevice corrosion conditions. In a previous work [24], the electrochemical behaviour of the martensitic SS in bulk electrolyte (neutral chloride solution) for different experimental conditions was investigated. To our knowledge, few studies have been reported in the literature concerning the crevice corrosion of a martensitic SS [25]. The chemistry of the electrolyte (pH and Cl^- concentration) plays an important role on the depassivation processes. In order to determine these critical values, anodic polarisation curves [26] and impedance measurements were obtained for different Cl^- concentrations and/or pH in deaerated conditions. Then, electrochemical impedance diagrams were obtained for the martensitic SS for various electrolyte thicknesses and for different exposure times in a thin-layer cell.

2. Experimental

2.1. Materials

The composition in weight percent of the X12CrNiMoV12-3 martensitic stainless steel was C = 0.12, Cr = 11.5, Ni = 2.5, Mo = 1.6, V = 0.3 and Fe to balance. The microstructure was completely martensitic with residual austenite content less than 1% [27].

Two types of electrochemical cell were used: a conventional three-electrode cell or a thin-layer cell. The conventional cell was used to determine the critical pH and Cl^- concentration values leading to the depassivation of the martensitic SS. The cell contained a platinum grid auxiliary electrode, a saturated calomel reference electrode (SCE) and a rod of the stainless steel of 1 cm^2 cross-sectional area, used as working electrode (rotating disk). The body of the rod was covered with a heat-shrinkable sheath leaving only the tip of the cylinder in contact with the solution. The electrode rotation rate was fixed at 100 rpm. A thin-layer cell, designed following previous work by Remita et al. [22], was used to investigate the crevice corrosion of the martensitic SS. Two configurations were used. First, a cylinder of the martensitic SS (10 mm in diameter) was facing a polymeric cylinder (30 mm in diameter) to obtain a restricted volume of electrolyte above the working electrode (Fig. 1a). Then, the polymeric cylinder was replaced by a martensitic SS cylinder (Fig. 1b) which allowed oxygen reduction on the external part of the cylinder to occur. The volume of the solution in the thin-layer cell varied from 565 μL to 70 μL (±14 μL) when the distance between the two cylinders decreased from 800 μm to 100 μm (±20 μm), respectively. The saturated calomel reference electrode and the platinum grid auxiliary electrode were located outside the confined zone.

Prior to any experiment, the stainless steel electrodes were abraded with successive SiC papers and diamond paste (grade 1000–3 μm), rinsed and sonicated in ethanol and finally dried in warm air.

As in our previous study [24], the electrolytic solution, used as reference, was prepared from deionised water by adding 0.1 M NaCl + 0.04 M Na_2SO_4 (reagent grade). Then, different solutions were prepared by changing the Cl^- concentration, the pH or both. The NaCl concentration varied from 0.1 M to 3 M. The pH of the electrolytic solution was decreased by addition of HCl (Normapur reagent) or H_2SO_4 (Carlo Erba reagent) from neutral pH to 1. In the conventional three-electrode cell, all the experiments were performed in deaerated conditions. The electrolyte was initially purged with nitrogen for 1 h then the working electrode was introduced into the cell. N_2 bubbling was maintained during the experiment.

2.2. Electrochemical measurements

Anodic polarisation curves were obtained under potentiodynamic regulation at a potential sweep rate of 0.6 V/h using a Solartron 1287 electrochemical interface. Electrochemical impedance measurements were carried out using a Solartron 1287 electrochemical interface connected with a Solartron 1250 frequency response analyzer. Impedance diagrams were obtained over a frequency range of 65 kHz to a few mHz with eight points per decade using a 15 mV peak-to-peak sinusoidal voltage. All the measurements were performed at room temperature.

After immersion in the confined media, the working electrode was rinsed with distilled water and ethanol and dried in warm air. The specimens were examined with an optical microscope (Olympus PMG3).

3. Results and discussion

First, to determine the critical conditions leading to depassivation of the X12CrNiMoV12-3 stainless steel, anodic polarisation curves and impedance measurements were performed in deaerated conditions for different NaCl concentrations and different pH (conventional three-electrode cell). Then, electrochemical measurements were performed in the thin-layer cell in the aerated reference solution. With the first configuration of the thin-layer cell (Fig. 1a), the impedance diagrams were obtained after different immersion times at the corrosion potential (E_{corr}) and for different electrolyte film thicknesses in order to characterize the behaviour of the martensitic SS in confined medium. The second configuration (Fig. 1b) was used to reproduce the conditions met during the crevice corrosion. The two martensitic SS electrodes were first electrically connected to induce the initiation and propagation of the crevice corrosion. However, it was not possible to observe the development of the crevice corrosion for long immersion times, as long as 30 days. Thus, the two martensitic SS electrodes were unconnected and the smaller electrode ($S = 0.78$ cm^2) was cathodically polarised at -1 V/SCE for 1 h to remove the oxide film [24].