# Corrosion behaviour of a martensitic stainless steel in a thin-layer cell

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## 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, the 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 process leads to a modification of the chemical composition of the electrolyte in the crevice with simultaneous acidification and increase of chloride ions concentration [3]. These new local conditions induce depassivation of the stainless steel and lead to severe corrosion. The crevice corrosion resistance of the stainless steels is strongly dependent on the passive films properties [4].

In a recent study, the electrochemical characterization of a martensitic stainless steel (X12CrNiMoV12-3) has been realized in bulk electrolyte (0.1 M NaCl + 0.04 M Na<sub>2</sub>SO<sub>4</sub> solution) [5]. It was shown that at the corrosion potential, the stainless steel was in the passive state and the corrosion process was controlled by the properties of the passive film formed during air exposure. When the samples were immersed in deaerated solution, the passive film was slightly modified, whereas it was altered both in composition and thickness during immersion in the aerated solution. After cathodic polarisation of the stainless steel, the oxide film was almost totally removed and the surface appeared to be uniformly active for oxygen reduction. The new passive film, formed at the corrosion potential, was enriched with iron species and less protective. Impedance diagrams allowed the characterization of both the oxide film (high-frequency range) and the charge transfer process (low-frequency range).

The next step, which constitutes the goal of the present study, was to investigate the crevice corrosion of the martensitic stainless steel in a thin-layer cell. Impedance measurements were performed under different thin electrolyte layers and for different exposure times. The results were analyzed by comparison with those obtained in bulk electrolyte [5].

## Experimental

### Material

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.

### Description of the set-up

The set-up used in this work was designed following the previous study of Remita et al. [6] (see Fig. 1). The originality of the device is that it is possible to minimize the errors of parallelism and the average thickness of the liquid film could be set with an accuracy of  $\pm 20 \mu m$ . The film geometry can be controlled by using a procedure based on high-frequency impedance measurements.

## Electrochemical measurements

The corrosive medium was prepared from distilled water by adding 0.1 M NaCl + 0.04 M  $Na_2SO_4$  (reagent grade). A saturated calomel electrode (SCE) and a large platinum grid were used respectively as reference and counter electrode. These two electrodes are located outside the confined area. Electrochemical impedance measurements were carried out using a Solartron 1287 electrochemical interface connected with a Solartron 1250 frequency response analyser. 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. The linearity of the system was checked by varying the amplitude of the ac signal applied to the sample. The electrochemical results were obtained from at least three experiments to ensure reproducibility. The impedance spectra were fitted by using electrical equivalent circuits with Z-view impedance software.



Fig. 1. Schematic view of the thin-layer cell device

# **Results and Discussion**

First of all, the experimental set-up was validated by performing impedance measurements on the martensitic stainless steel (working electrode was the cross-section of a metallic cylinder (10 mm in diameter)) facing a polymeric cylinder (30 mm in diameter) which insures the confinement of the electrolyte layer above the steel (Fig. 1). The impedance diagrams obtained for different immersion times up to 70 h are relatively similar and are characterized by a single time constant (Fig. 2). A slight increase of the impedance modulus is observed when the immersion time increases. Similar results have been obtained in bulk deaerated electrolyte. Thus, it can be concluded that in the thin-layer cell, the oxygen was consumed and the martensitic stainless steel remains in the passive state.

Then, the polymeric cylinder was replaced by a stainless steel sample which allows the oxygen reduction on the external part of the cylinder to occur. The working electrode became the anode. The impedance diagrams obtained for three immersion times are given in Fig. 3. In this case, the diagrams are characterized by two time constants which are significantly modified between 2 h and 18 h of immersion. The impedance modulus is lower than that measured in the first configuration (Fig. 1) and it decreases progressively with increasing immersion time. The modification of the high-frequency part was attributed to an alteration of the passive film and the decrease of the impedance modulus was linked to the development of the crevice corrosion which was clearly visible after the experiment.



**Fig. 2.** Electrochemical impedance diagrams obtained for the martensitic stainless steel in the thin layer cell (electrolyte thickness =  $100 \mu$ m) at the corrosion potential for different immersion times in a 0.1 M NaCl + 0.04 M Na<sub>2</sub>SO<sub>4</sub> solution (the upper part of the cell was a polymeric cylinder)



Fig. 3. Electrochemical impedance diagrams obtained for the martensitic stainless steel in the thinlayer cell (electrolyte thickness =  $80 \ \mu\text{m}$ ) at the corrosion potential for different immersion times in a 0.1 M NaCl + 0.04 M Na<sub>2</sub>SO<sub>4</sub> solution (the upper part of the cell was a stainless steel disk)

#### Conclusions

A thin-layer cell was developed which allowed the crevice corrosion of the martensitic stainless steel to be reproduced. The influence of the immersion time and the electrolyte layer thickness was clearly shown.

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#### References

- 1. D. Thibault, P. Bocher, M. Thomas, J. Mater. Process. Tech. 209 (2009) 2195.
- 2. X.P. Ma, L.J. Wang, C.M. Liu, S.V. Subramanian, Mater. Sci. Eng. A 539 (2012) 271.
- 3. J.R. Oldfield, W.H. Sutton, Br. Corros. J. 13 (1978) 13.
- 4. P. Schmuki, S. Virtanen, H.S. Isaacs, M.P. Ryan, A.J. Davenport, H. Böhni, T. Stenberg, J. Electrochem. Soc. 145 (1998) 791.
- 5. S. Marcelin, N. Pébère, S. Régnier, submitted to Electrochim. Acta (March 2012).
- 6. E. Remita, E. Sutter, B. Tribollet, F. Ropital, X. Longaygue, C. Taravel-Condat, N. Desamais, *Electrochim. Acta* 52 (2007) 7715.