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Electrochemical impedance spectroscopy for the detection of stress corrosion cracks in aqueous corrosion systems at ambient and high temperature

Rik-Wouter Bosch

SCK-CEN, Belgian Nuclear Research Centre, Boeretang 200, B-2400 Mol, Belgium

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Abstract

Electrochemical impedance spectroscopy (EIS) has been used as a tool to detect stress corrosion cracking in a stainless steel sample exposed to an aqueous environment at ambient and high temperature. A model has been developed to describe the impedance of a cracked surface. This model could distinguish between a flat electrode surface and an electrode surface with cracks. To test this technique, three case studies were considered: (1) Slow Strain Rate Tests (SSRT) on sensitised Type 304 SS specimen in a 5 N H₂SO₄ + 0.1 M NaCl solution at room temperature, (2) constant load tests on Type 304 SS in a boiling (± 110 °C) acidified sodium chloride solution, and (3) Slow Strain Rate Tests (SSRT) on Type 304 SS in an oxygen containing solution of 0.01 M Na₂SO₄ at 300 °C.

EIS measurements were always performed simultaneously on two identical samples: one stressed with a SSRT or a constant load test and one free of stress. Kramers Kronig Transformations have been used to validate the experimental data obtained with the EIS measurements. It was shown that the phase shift between the two samples could be related to the stress corrosion cracking process. Analysis of the fracture surfaces confirmed that stress corrosion cracks were formed in all three cases.

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Keywords: Stress corrosion cracking; EIS; Stainless steel; Corrosion monitoring

E-mail address: rbosch@sckcen.be (R.-W. Bosch).

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Nomenclature

C_{crack}	double layer capacity at the crack tip, $C_{\text{crack}} = C_{\text{dl}}\pi r^2$ (F)
C_{dl}	double layer capacity (F/mm ²)
C_{surface}	double layer capacity of the outer surface of the working electrode (F)
C_{wall}	double layer capacity of the crack wall per unit length, $C_{\text{wall}} = C_{\text{dl}}2\pi r$ (F/mm)
e	potential along the crack (V)
E_L	potential at the crack tip (V)
i	current along the crack (A)
L	crack length (mm)
r	crack radius (mm)
R_{crack}	polarisation resistance at the crack tip $R_{\text{crack}} = \frac{R_{\text{passive}}}{\pi r^2}$ (Ω)
R_{ohm}	ohmic resistance (Ω)
R_{passive}	polarisation resistance of passive stainless steel (Ωmm^2)
R_{sol}	solution resistance of the solution in the crack per unit length (Ω/mm)
R_{surface}	polarisation resistance of the outer surface of the working electrode (Ω)
R_{wall}	polarisation resistance of the crack wall per unit length, $R_{\text{wall}} = \frac{R_{\text{passive}}}{2\pi r}$ (Ωmm)
z	distance along the crack (mm)
Z_{crack}	impedance of the total crack (Ω)
Z_{cracktip}	impedance of the crack tip (Ω)
Z_{wall}	impedance of the crack wall (Ωmm)
κ	conductivity of the electrolyte solution ($\Omega^{-1} \text{mm}^{-1}$)

1. Introduction

Impedance measurements have only been used occasionally for the investigation of stress corrosion cracking phenomena. Oltra et al. [1] have used a transmission line, similar to the cylindrical pore model developed for the potential distribution in porous electrodes of de Levie [2], to model the impedance of a stress corrosion crack. Petit et al. [3] have used impedance measurements during Slow Strain Rate Tests (SSRT) of Type 304 SS in boiling 44% MgCl₂ solution. They measured the phase at a particular frequency during the tests and try to correlate crack initiation to changes in this phase. We have also used this approach in previous work where it was shown that an evolution in the phase of the impedance at certain frequencies could be linked to the occurrence of stress corrosion cracking [4].

In this paper we will summarise the results of stress corrosion cracking detection with impedance measurements of three different stress corrosion cracking systems. First however we will use a mathematical model of the crack impedance to investigate the relationship between the crack length, the perturbation frequency and the outer surface area of the metal specimen that holds the (possible) stress corrosion crack. For this model the transmission line model is used and extended to model the

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