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Crevice corrosion behaviour of superaustenitic stainless steels: Dynamic electrochemical impedance spectroscopy and atomic force microscopy studies

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ABSTRACT

Potentiodynamic anodic polarisation and dynamic electrochemical impedance spectroscopic (DEIS) measurements were carried out for 316L SS, alloy 33 and alloy 24 in natural sea water in order to assess their crevice corrosion resistance. DEIS measurements were performed from open circuit potential to dissolution potential. It was shown that the impedance measurements in potentiodynamic conditions allow simultaneous investigation of changes in passive layer structure. The impedance spectra of various potential regions were also discussed. The surface morphology of the alloys after crevice corrosion studies were studied using optical microscope and atomic force microscopy (AFM).

1. Introduction

Stainless steels (SS) are being increasingly used as a structural material in marine and petrochemical applications. This is mainly due to their high corrosion resistance, high strength and toughness. However, in many applications the SS structures have fittings that leads to crevices due to their design for instance, between threaded or riveted connections, spot welded lap joints, gaskets and flanges that make these structures prone to crevice corrosion. Crevice corrosion has been the subject of many investigations as a result of its wide spread occurrence and its destructive nature [1,2]. At the end of the 70s Oldfield and Sutton [3,4] has been shown that in chloride environment the solution inside the crevice undergoes hydrolysis reaction leading to an increased acidity and chloride concentration in occluded volumes, which can eventually lead to rapid passive film break down. The IR drop has also been found to influence the crevice corrosion of stainless steel [5], grain boundary corrosion [6], corrosion under organic coatings [7] and corrosion within pores of sintered metals [8]. To avoid crevice corrosion in stainless steel material, counter measures such as surface modification, reducing the aggressiveness of the environments, bulk alloying etc have been undertaken earlier [9–11]. One of the methods to improve the crevice corrosion resistance in the given environments by development of superaustenitic stainless steels, addition of steels with higher chromium, molybdenum and nitrogen contents for higher resistance to localised corrosion. Superaustenitic stainless steels are used for very highly corrosive environments like chemical processing equipment, critical seawater and severe brackish water-handling systems, desalination systems, plate heat exchangers, municipal waste incineration systems and chlorine and chlorine dioxide pulp bleaching systems. Moreover, the passive film behaviour formation during the crevice corrosion that occurs in stainless steel still needs further clarifications and better understanding.

Various electrochemical techniques are being used to asses the crevice corrosion process. Among this, electrochemical impedance spectroscopy (EIS) is the much sought after technique as it provides information on the mechanism and reaction kinetics of the electrode. In the classical EIS technique the system can be considered as a stationery one, in which case the investigated process should remain constant during the time of full impedance experiment [12]. During the crevice corrosion process the nature of the passive film on the metal surface may be varied with respect to its environment. In such a case, the stationary condition for the investigated system is not fulfilled and the classical EIS fails. This disadvantage in using the classical EIS technique initiate us to carry out Dynamic Electrochemical Impedance Spectroscopy, which can possibly follow the passive layer changes on the metal surface during the crevice corrosion process. Darcowicki et al. [13–15] were developed the Dynamic Electrochemical Impedance technique and investigated the pitting corrosion, pit pre-initiation state and transports of organic coatings.

In the present work, the different composition of stainless steels namely 316L SS, alloy 33 and alloy 24 were used to evaluate the crevice corrosion resistance by using potentiodynamic polarisation. The dynamic electrochemical impedance spectroscopy measurements were carried out to investigate the passive film behaviour under linear potential change for these alloys. The surface morphology

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Table 1
Chemical composition of investigated alloys (wt.%).

Alloy	Main alloying elements (wt.%)					
	Cr	Ni	Mo	N	C	Mn
316L SS	17.2	12.60	2.40	0.02	0.030	1.95
Alloy 33	32.85	30.95	1.67	0.39	0.007	0.64
Alloy 24	24.20	17.70	4.34	0.46	0.012	6.14

of the passive film after the crevice test were analysed by using optical microscopy and AFM technique.

2. Experimental

The samples were received from VDM corporation, USA and their chemical composition of 316L SS, alloys 33 and 24 are given in Table 1. The samples geometry for crevice corrosion experiment are also given in Fig. 1. The size of the sample were cut out the dimensions of 50 × 50 × 3 mm with 10 mm hole in the centre were cut out, and wet polished with emery paper up to 600. The specimens were then washed with water, degreased with acetone followed by alcohol and then air dried. Multicrevice corrosion test assembly was prepared based on the standard guide for crevice corrosion test, ASTM G78. The crevice former was a polyacetal resin rings, which had 20 teeth of dimensions 2 × 2 mm, two of these rings were pressed onto the specimen at a torques of 8.5Nm with titanium bolt and a nut, so that 20 small crevice sites were formed on each side of the specimen. The bolt was electrically insulated from the specimens using a polytetrafluoroethylene tape, which was immersed in the electrolyte. A conventional three electrode cell was used for all the electrochemical measurements. A saturated calomel electrode (SCE) was used as a reference electrode, platinum foil acts as a counter electrode and the test material as the working electrode. Natural sea water collected from the costal area of Chennai, India served as the electrolyte. The compositions of the natural sea water are given in Table 2.

Potentiodynamic polarisation studies were carried out for the test specimens in natural sea water. The potentiostat (model PGSTAT 12, AUTOLAB, the Netherlands B.V) controlled by a personal computer and the software (GPES Version 6.0) was used for conducting the polarisation experiments. The potential was applied on the working electrode at a scan rate of 1 mV s^{-1} In order to test the reproducibility, the experiments were performed in triplicate.

Table 2
The major chemical composition of the sea water used in the present study.

Element	Composition (g/lit)
Cl	19.00
Na	10.50
Mg	1.35
S	0.88
Ca	0.40
K	0.38
Br	0.06
C	0.02

DEIS measurements were carried out using a Frequency Response Analyser (FRA), which included a potentiostat model PGSTAT 12. Impedance spectra were acquired from the corrosion potential to the dissolution region with a step potential of 20 mV in the frequency range of 55 kHz–0.1 Hz with a 10 mV amplitude sine wave generated by the FRA.

After the crevice corrosion experiments the specimens were characterised using stereoscopic microscope (Macscope – Z, India) equipped with a variable removable lens. Micrographs were captured using a digital camera and triplicate experiments were conducted capturing 6 images per sample. The surface morphology was recorded by AFM using a nanosurf easy scan 2 (Nanosurf AG, Grammetstrasse 14, CH-4410 Liestal, Switzerland). The images were acquired by contact mode, using silicon nitride cantilevers with a spring constant of 0.15 N/m and the resonance frequency was 13 kHz. All images were recorded under air atmosphere at room temperature.

3. Results and discussion

3.1. Potentiodynamic polarisation studies

Fig. 2 shows the potentiodynamic anodic polarisation curves of 316L SS, alloys 33 and 24 in natural seawater. The critical crevice potential for the reference material was 236 mV, whereas the critical crevice potentials for alloys 33 and 24 were found to be 854 mV and 932 mV, respectively. The above result clearly reveals that the alloys 33 and 24 exhibit a higher crevice corrosion resistance in natural seawater as compared to stainless steel.

Further, this behaviour can be attributed to the higher amounts of alloying elements, namely, nickel, chromium, molybdenum and

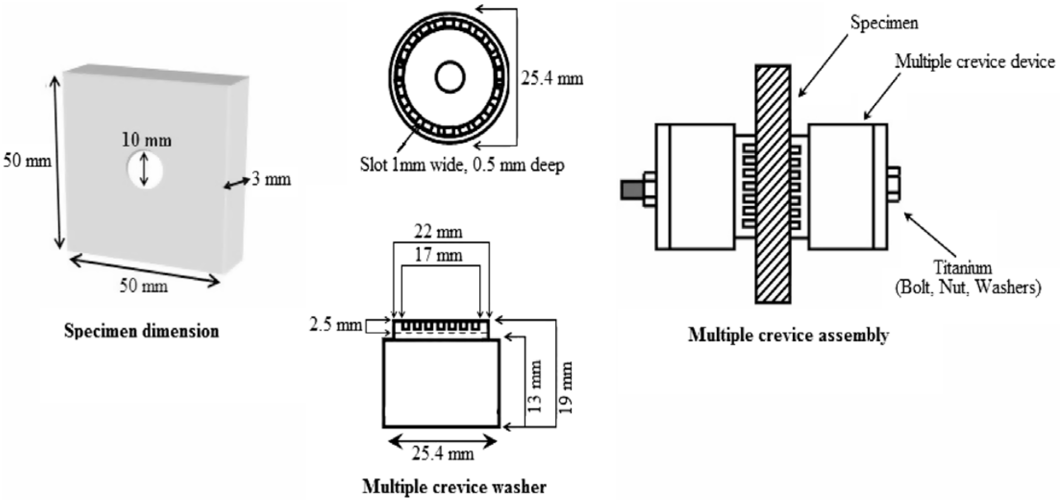

Fig. 1. The geometry of the specimens and crevice corrosion assembly.