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The effect of zinc addition in stress corrosion cracking initiation in nickel alloy 600 in simulated PWR primary water

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Abstract

Stress corrosion cracking (SCC) is one of the corrosion-related causes to premature fracture of structures. SCC is a term used to describe service failures in engineering materials that occur by slow, environmentally induced crack initiation and propagation. The structural failures can occur in a sudden and unexpected way, causing catastrophes with serious social, economical and environmental consequences. The observed crack propagation is the result of the combined and synergistic interaction of mechanical stress and corrosion reactions. It affects materials that present resistance to general corrosion such as austenitic stainless steel and aluminum, nickel and titanium alloys. The nickel alloy 600 is susceptible to SCC in high temperature hydrogenated water, environment found in primary water of pressurized water reactors (PWR), this phenomenon is also known as PWSCC (Primary Water Stress Corrosion Crack). Addition of zinc to the reactor coolant system has been used as a mean to effect radiation dose reductions. The effectiveness of zinc in contributing to reduced radiation fields in PWR is now well established, with positive results observed in PWR's. However, zinc is also added as an approach to mitigate the occurrence or severity of PWSCC of alloy 600. The purpose of the present investigation was to evaluate the effect of zinc addition on the corrosion resistance of the alloy 600 using the crack initiation tests with U-bending samples (ASTM G30 standard) in a simulated PWR condition with and without zinc addition. The influence of zinc on the corrosion susceptibility of alloy 600 was evaluated by electrochemical impedance spectroscopy (EIS) and scanning electron microscope (SEM).

Keywords: cracking initiation; nickel alloy 600; zinc; electrochemical impedance spectroscopy.

1. INTRODUCTION

Corrosion is a deterioration process that affects materials and it is caused by chemical and/or electrochemical reactions allied or not to mechanical stresses. Being an expontaneous process, corrosion continuously affects metallic materials and their performance in service is also affected (1). Stress corrosion cracking (SCC) is a form of material degradation associated to applied or residual mechanical stresses in a specific corrosive environment and occurs in materials that have high resistance to general corrosion (2). Stress corrosion cracking is one of most severe damage mechanisms influencing the lifetime of components in the operation of nuclear power plants like piping, pressure vessels and steam generators interns (3). It

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causes cracks in the components which eventually can fail. Nickel alloys are used in some components of pressurized water reactors (PWR), like the pressure vessel control rods and filler metal in dissimilar welds due to their mechanical properties and resistance to corrosion (8). Figure 1 shows a schematic of the pressure vessel where this application is found. Nickel alloy 600 and its weld metals 82 and 182 were selected to use in nuclear reactors due to their high corrosion resistance. However after many years of operation they presented signs of susceptibility to SCC (4). Addition of zinc to the reactor coolant system of nuclear power plants has been used as a means to effect radiation dose reductions.
The literature indicates that the presence of zinc in oxide films formed on alloy surface decreases the SCC initiation. This work is part of a research project that aims to evaluate the effect of zinc in the crack initiation by SCC of alloy 600 in PWR primary water environment. Initial results of this study are presented in this work.

2. MATERIAL AND METHODS

The material to make specimens was a rod (108 mm x 21 mm x 31 mm) of Inconel 600 (mill-annealed), shown in Figure 2. Its chemical composition is in Table 1.

2.1 CUT AND SETUP OF SPECIMENS

The specimens were made according to ASTM G 30-97 standard, which is a guide for SCC tests using U-bend specimens (5). The Inconel 600 rod was cut in plates of 100 mm x 9 mm x3 mm, which were later drilled at the both ends (diameter = 7 mm) to put screws and insulators, according to detail shown in Figure 2. The cutting was performed by electroerosion, a technique that produces little modification in the material microstructure.

2.2 SURFACE FINISHING

The Inconel 600 plates were grinded with SiC paper (grit sizes 180; 280; 320; 400; 500; 600; 1200; 2000) and polished with diamond paste (6 µm; 3 µm; 1 µm). Figure 3 shows the final surface of the plates.

2.3 U-BENDS MAKING OF

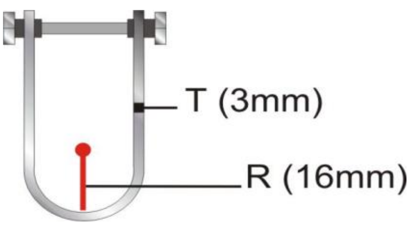
The Inconel plates were bended in U shape using a bender as shown in Figure 4. They were kept in U shape by means of stainless steel screws so creating a stress intensity area (5). To avoid formation of a galvanic cell between Inconel and stainless steel during the corrosion tests (1), the plates were insulated from the screws by means of oxidized zircaloy rings, shown in Figure 7.

The total deformation (E) of the specimens was 9.3 %, which was calculated by the equation 1*.

$$E = T / 2R \quad when\ T < R \qquad 1^*$$

where:

T = plate width
R = specimen radius



The higher stresses surface area of the U-bend specimens was later examined by SEM to look for cracks caused by bending. Figure 5 shows images of the surface area where one can see that no cracks are present. The deformation of the material caused the formation of bands in different directions with the appearance of an orange peel, when observed by naked eye.

2.4 SCC FACILITY

Figure 6 shows the facility used in this work. It is used to do accelerated SCC tests in laboratory scale. It comprises an autoclave, instruments to measure temperature and pressure and a water tank where the desired water chemical composition can be adjusted.

2.5 SIMULATED PWR PRIMARY WATER

The facility permits to simulate the operational condition of primary water PWR. The water chemical composition used in the tests is shown in Table 2 along with pressure and temperature values. Prior to beginning the test dissolved oxygen was removed from water by bubbling it with nitrogen. Afterwards a hydrogen overpressure of 3 bar was used in the tank.

The specimens were placed attached to a frame and hold by the autoclave cover. Figure 7 shows the setup.

2.6. IMPEDANCE MEASUREMENTS

After the exposure time in the autoclave and the examination of the specimens, their impedance was measured at 30 °C in 0.1 mol.L^{-1} sodium sulphate solution. The exposed area of the specimen was 4 cm^2. The conventional three electrode cell was used with Ag/AgCl as reference and Pt as auxiliary electrode. The frequency range was 10 kHz to 10 mHz with an amplitude of 5 mV rms. For each specimen an average of four measurements was carried out. An Autolab PGSTAT20 potentiostat was used.

3. RESULTS AND DISCUSSION

On the first test that was carried out without zinc, 5 U-bend specimens were submitted to PWR water for 1272 h. On the second test, performed in 80 ppb zinc containing water, also 5 U-bend specimens were tested for 1296 h. After the time of exposure the specimens were withdrawn from the autoclave and cleaned in deionized water by ultra sonic bath.
In looking for cracks on the specimens the following procedure was used:

- Examination of the specimens in optical microscope;
- Marking of the probable areas with cracks;
- Examination of the probable areas with cracks by SEM;
- Determination of crack size.

The examination of the specimens by optical microscope was not sufficient to confirm the presence of a crack on the specimen. There were observed some regions where microcracks

could possibly be present. This was later confirmed by SEM in specimens exposed to water without zinc.
There were found microcracks in all of the U-bend specimens exposed to water without zinc. The average crack size was 10 µm. Figure 8 show images of the cracks.

Samples exposed to 80 ppb zinc containing water presented a more compact and less porous oxide film, what made it difficult to find cracks on the specimens. Figure 9 shows SEM images of the oxide film.
The electrochemical impedance of the specimens was measured after the exposure time. The results presented some dispersion what made the evaluation difficult. However after selection of data that presented less dispersion, it was possible to verify that specimens exposed to zinc containing water had higher corrosion resistance. Figure 10 shows an example of Nyquist plot obtained from selected data. We can see that the specimen exposed to zinc had higher impedance.

The data were fit to the simple model R(QR) which refers to an equivalent circuit with the solution resistance Rs in series with a capacitance expressed as a CPE (constant phase element) and the polarization resistance Rp in parallel with the CPE as shown below. Table 3 presents the parameters obtained from fitting the selected data to this model.
From Table 3, it can be seen that the specimens exposed to zinc presented lower capacitance and higher polarization resistance. This indicates that those specimens have higher corrosion resistance than those exposed to water without zinc.

4. CONCLUSIONS

- U-bend specimens of nickel alloy 600 exposed to simulated PWR water without zinc presented cracks preferentially at the place of higher deformation. The average crack size was 10 µm.
- Cracks were not found in specimens exposed to simulated PWR with zinc. A compact and less porous oxide film was detected by SEM examination.
- The results show that zinc affected the morphology of oxide films formed on alloy 600 U-bend specimens.
- Impedance data confirm the positive effect of zinc in increasing corrosion resistance.

5. ACKNOWLEDGEMENTS

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7. FIGURES END TABLES

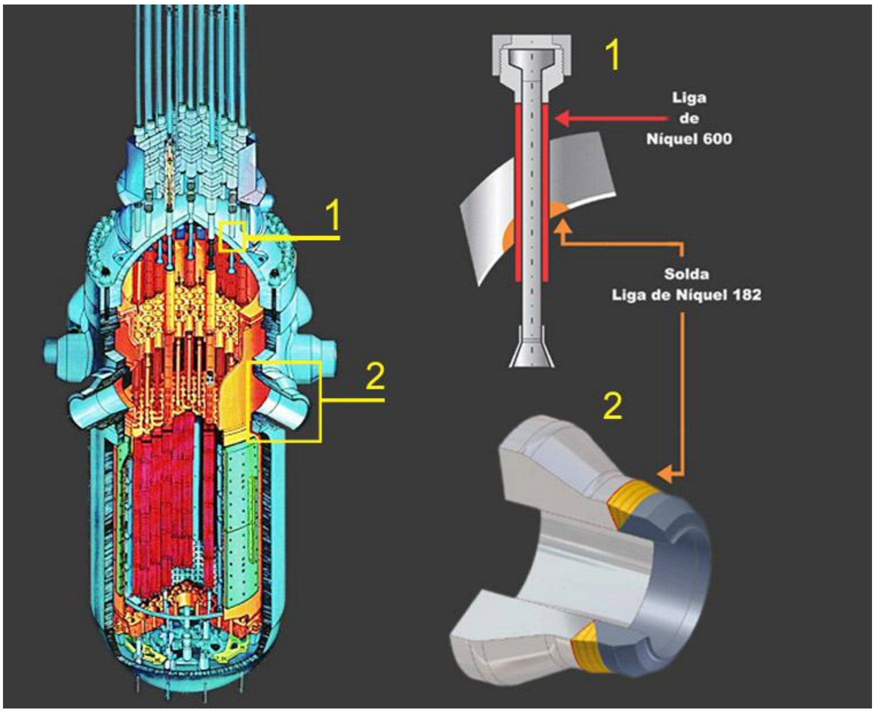

Figure 1. Schematic of the pressure vessel showing the location of nickel alloys.

C	0.042	**Mn**	0.22	**Al**	0.08	**Si**	0.18	**Cr**	15.61
P	0.008	**S**	0.0002	**Ti**	0.20	**Ni**	75.05	**Nb**	0.20
Cr	15.61	**Co**	0.10	**Cu**	0.03	**Fe**	8.81		

Table 1. Chemical composition of Inconel 600 (%wt).

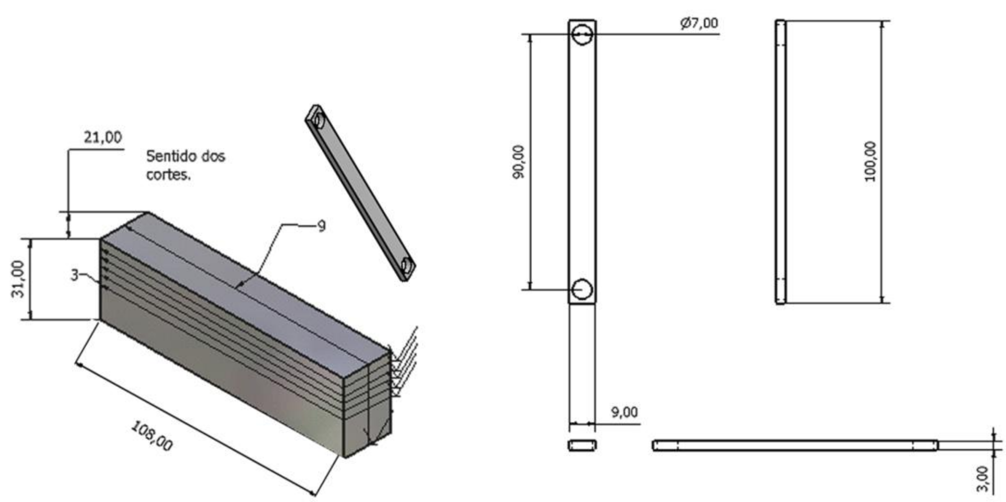

Figure 2. Schematic of the Inconel 600 rod. In detail, the specimen dimensions.

Figure 3. Inconel 600 plates polished up to 1 µm.

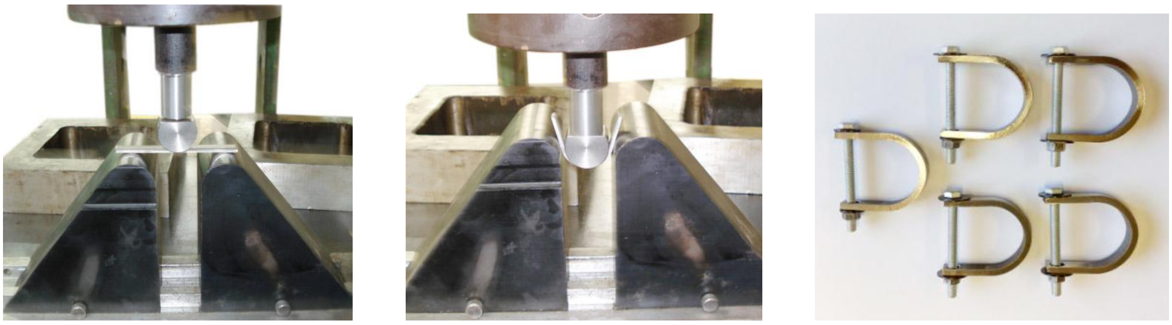

Figure 4. Bending of Inconel plates on the left. On the right the U-bend specimens.

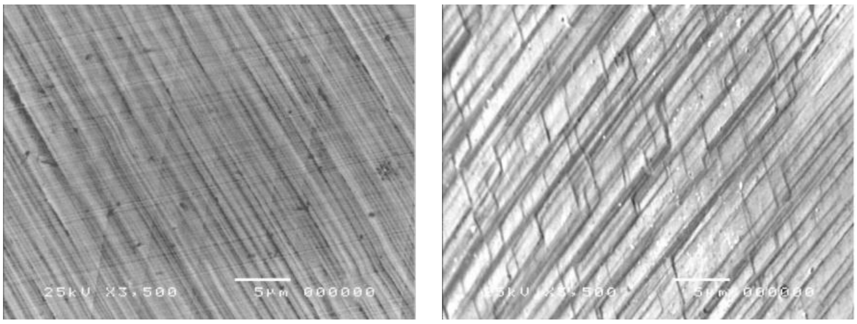

Figure 5. SEM images of the U-bend specimens taken in the area of higher deformation.

Figure 6. Facility for SCC tests.

PWR environment	
Bore	1200 ppm
Lithium	2.2 ppm
Oxygen	5 ppb
Pressure	140 atm
Temperature	325ºC

Table 2. Water chemical composition and operational conditions used in the tests.

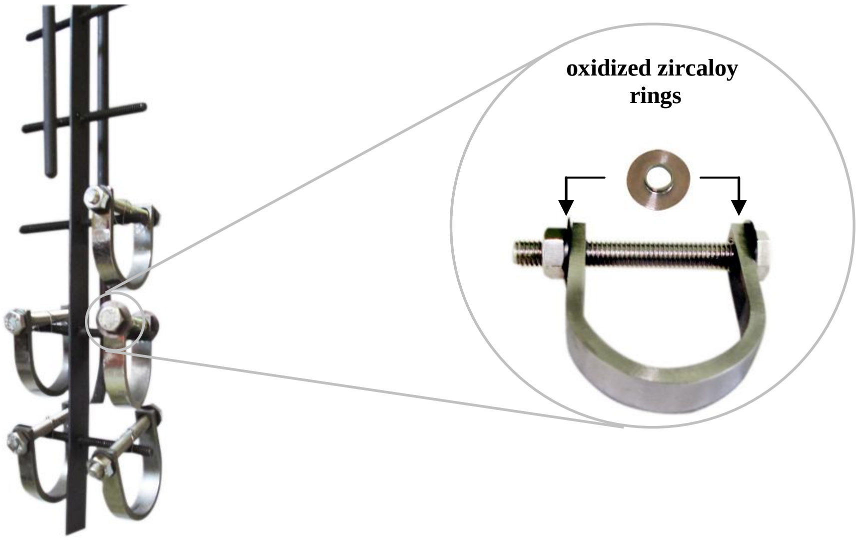

Figure 7. Setup of specimens in the frame. In detail the oxidized zircaloy rings used as insulators.

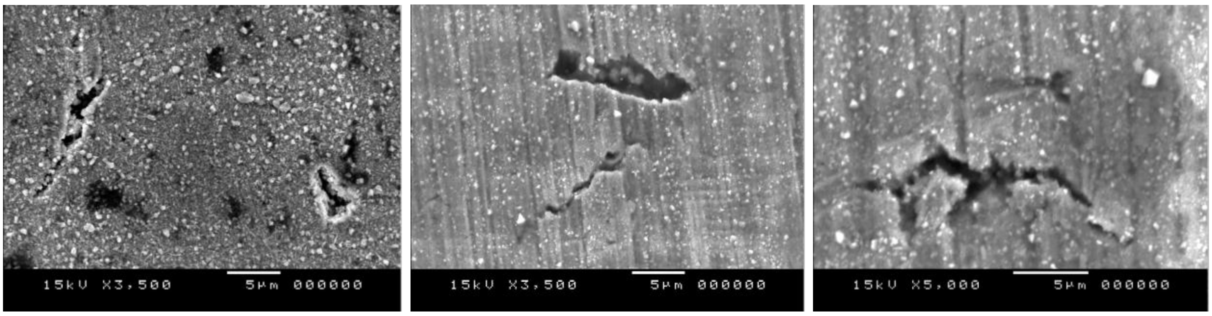

Figure 8. SEM images of microcracks found in the U-bend specimens exposed to water without zinc, in the place of higher deformation.

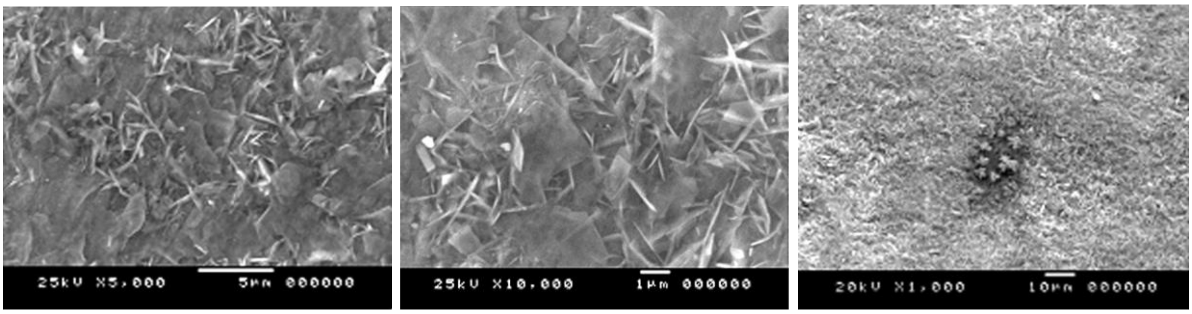

Figure 9. SEM images of oxide film on specimens exposed to zinc containing water, in the place of higher deformation.

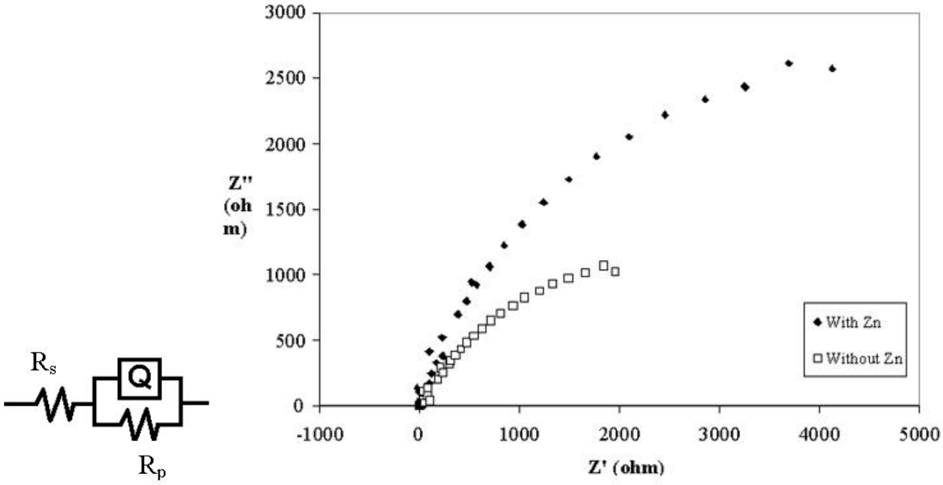

Figure 10. Impeadance data in Nyquist plot for specimens exposed to water with zinc or without zinc.

Parameter	Without Zn	With Zn
R_s (ohm)	2.96	2.30
$Q\text{-}Y_o$ ($S.s^n$)	0.001663	0.000822
Q-n	0.780	0.747
R_p (ohm)	1722	4475

Table 3. Parameters obtained by fitting the data to the model R(QR).

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