Anti-Corrosion Methods and Materials

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Article information:

Permanent link to this document: http://dx.doi.org/10.1108/00035591211265550

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Corrosion pit growth on austenitic stainless steels in chloride containing solution:
a quantitative approach

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Abstract
Purpose – The purpose of this paper is to quantitatively assess the pit growth rate on AISI 304L and AISI 316 austenitic stainless steels in natural seawater and 3.5 wt.% NaCl solutions through electrochemical measurements during the potentiostatic growth of pits.

Design/methodology/approach – A quantitative characterisation was carried out based on chronoamperometric measurements. The volume of dissolved metal per pit was calculated from the charge registered and Faraday’s law, considering both, hemispherical and semi-elliptical pit shapes and the density of the steels. Empirical growth laws for maximum pit depth as a function of polarisation time were obtained and compared with pits volumetric profile obtained from optical microscopy analysis and mechanical removal of material on both steels.

Findings – Electrochemical-based calculations of localised metal dissolution per pit present acceptable fit with the real volume of dissolved metal on hemispherical pits.

Originality/value – The paper presents the quantitative relationship of the corrosion pit growth rate of stainless steels in chloride containing solution determined by chronoamperometry (electrochemical technique) through the Faraday law’s, with the mechanical removal of material (pit profile) through the density of metal.

Keywords Stainless steel, Corrosion, Chloride, Electrochemistry, Pitting

Paper type Research paper

1. Introduction
Pitting corrosion is a localised electrochemical dissolution process that in some cases can induce catastrophic failure of passive metals. This form of localised attack can be considered as a case where only small areas of the metal surface undergo localised attack whilst the rest of the surface is largely unaffected and remains passive. Pitting is a particularly insidious form of corrosion because the extent of metal dissolution reaction is small but the attack is rapid and penetrates into the metal. The result of the rapid perforation of thin metal sections can induce leakage of fluid, for example, or alternatively, pitting to cracking transition may occur with consequent crack nucleation and growth leading to brittle catastrophic failure (Turnbull et al., 2006; Kondo, 1989). The location of pits on metals that develop passive films is often unpredictable with pits tendency to randomly disperse on the metal surface, though there is evidence for preferential location at non-metallic inclusions (Isaacs, 1989; Macdonald, 1992; Burstein et al., 2004; Djoudjou et al., 1993).

The initial event in localised corrosion of stainless steels (SS) is passivity breakdown, followed by pit nucleation, growth, and in some cases repassivation of these corrosion resistant metals (Burstein et al., 1993; Pistorius and Burstein, 1992). Pitting corrosion can occur when a local breakdown of the passive film takes place in an aqueous solution. Active dissolution of the freshly exposed metal takes place and a microscopic corrosion pit is formed. When the passive film does not recover sufficiently rapidly, the tiny pit continues to grow, leading to an active macroscopic pit. Nevertheless, in most cases, regeneration of the passive film occurs far more often than formation of an active macropit (Pistorius and Burstein, 1992). This suggests that only under specific disadvantageous conditions will repassivation fail to occur.

The location of pits is, to some extent, defined by the microstructure of the alloy and the geometry of the system. In chloride containing aqueous solutions, the uniform corrosion rate of SS in the passive state is insignificant, i.e. 0.15-15.0 μm per year (Isaacs, 1989; Djoudjou et al., 1993). However, pitting corrosion of this type of alloy is very common in environments where the local dissolution rate of metal can be up to 12 mm per year (Djoudjou et al., 1993).

According to Burstein and Pistorius (Burstein et al., 1993, 2004; Pistorius and Burstein, 1992), the initiation of pitting corrosion in SS takes place in two successive steps. The first step
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is nucleation: breakdown of the passive film on a microscopic scale. This process involves small and sudden increments of anodic current that are characterised by current spikes, leading to oxidation and dissolution of less than 0.01 μm² of metal. The nucleation process is unstable and in most cases it will stop by the regeneration of the passive film. Another possibility is that a nucleation event develops into the second stage of initiation, i.e. the metastable pit growth. During this stage, a gradual and bigger increase of the anodic current takes place. This stage stops if repassivation of the micro-pit occurs. A volume of up to bigger increase of the anodic current takes place. This stage is the regeneration of the passive film. Another possibility is that a nucleation process is unstable and in most cases it will stop by oxidation and dissolution of less than 0.01

It continues by an autocatalytic mechanism. The rapid dissolution of sulphide inclusions, these corelated models of pit growth in terms of volume of dissolved metal per pit and maximum pit depth (MPD) from electrochemical measurements. Pits generated on both stainless steel alloys at open circuit potential in FeCl₃ presented similar morphology and growth rate law to potentiostatically generated pits.

2. Experimental

2.1 Materials

Samples of AISI 304L and AISI 316 austenitic SS in the as received condition (annealed), were used in this work. The chemical composition of both steels is presented in Table I.

Specimens of 1 cm² surface area were embedded in Bakelite. Prior to the electrochemical tests the specimens were ground with up to 600 grit (P 1200) emery papers, rinsed with distilled water, degreased with acetone and air dried.

2.2 Determination of corrosion potential (Ecorr) and pitting potential (Epit)

Potentiodynamic polarisation tests were conducted using a conventional three-electrode electrochemical cell with a saturated calomel electrode (SCE) as reference electrode, a graphite bar as auxiliary electrode and stainless steel samples as working electrodes. All potentials in this study are quoted vs the SCE. Measurements were conducted at room temperature (25 ± 1°C) with the cell open to the air in electrolytes of different conductivity as shown in Table II. The NaCl and FeCl₃ solutions were prepared with analytic grade chemicals and distilled water.

Potentiodynamic polarisation involved the application of a cathodic overpotential (νc) of 250 mV vs OCP, from which the potential sweep initiated to the anodic direction at a scan rate of 10 mV s⁻¹. A criterion of sudden current density increase of two orders of magnitude was considered to determine the Epit. Potentiodynamic polarisation was performed using a computer controlled Potentiotstat/Galvanostat PAR EG&G model 273A.

Table I Chemical composition (wt.%.) of the steels

<table>
<thead>
<tr>
<th>Stainless steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Co</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
<td>0.019</td>
<td>0.39</td>
<td>1.40</td>
<td>0.025</td>
<td>0.001</td>
<td>18.30</td>
<td>–</td>
<td>9.07</td>
<td>0.12</td>
<td>0.054</td>
</tr>
<tr>
<td>AISI 316</td>
<td>0.020</td>
<td>0.49</td>
<td>1.28</td>
<td>0.029</td>
<td>0.003</td>
<td>17.13</td>
<td>2.09</td>
<td>11.19</td>
<td>0.16</td>
<td>0.032</td>
</tr>
</tbody>
</table>

(Laycock and Newman, 1997). Further support of the importance of salt film formation was obtained by Frankel from studies on metastable pitting of SS where covered pits were formed during metastable growth (Frankel et al., 1987). From the evaluation of single current transients and assuming a hemispherical pit shape the same author showed that most of the pits grow at constant current density (Frankel et al., 1987; Frankel, 1998). The literature related to the pitting corrosion of SS has been much more focused on the initiation and propagation mechanisms than on the dissolution rate. The characterisation of the localised metal dissolution rate is of paramount importance for real applications in which stainless steel components and structures are in contact with chloride containing environments that induce pitting and crevice corrosion. This work was directed towards the characterisation of the dissolution rate of potentiostatically generated of pits on austenitic SS (AISI 304L and AISI 316) in chloride containing solutions. The main objective was to determine the empirical growth rates of pits in terms of volume of dissolved metal per pit and maximum pit depth (MPD) from electrochemical measurements. Pits generated on both stainless steel alloys at open circuit potential in FeCl₃ presented similar morphology and growth rate law to potentiostatically generated pits.
The tests were carried out three times in each electrolyte. Results obtained from this stage indicated that the most active E_pit for both steels was obtained from tests in high conductivity electrolytes (3.5 percent NaCl solution and natural seawater).

2.3 Electrochemical generation of pits
Corrosion pits were generated on both steels in 3.5 percent NaCl solution and natural seawater, which were the most aggressive electrolytes, and also because preliminary tests indicated minimum scattering during pit generation compared to tests in electrolytes with lower conductivity. The methodology used for the generation and growth of corrosion pits, as well as for the determination of the pit depth, followed the work described by Zhou and Turnbull (1999). The sequence of potentiostatic polarisation is shown schematically in Figure 1 as a plot of potential vs time, as reported also by González-Sánchez (2002).

From the results of preliminary corrosion pit generation tests in which different combinations of anodic potential/time were applied, the most reproducible combination to induce controlled pit nucleation and stable growth was determined. The conditions of potentiostatic anodic polarisation as a function of time for corrosion pit generation and controlled growth are presented in Table III for both SS in natural seawater and 3.5 percent NaCl solution.

The events promoted by the anodic polarisation sequence shown in Figure 1 have been explained elsewhere (Zhou and Turnbull, 1999; González-Sánchez, 2002). Potentiostatic pit growth was carried out for periods of 5, 10, 15, 20, 30, 40, 50 and 60 min in order to get pits with different depths. Determination of the mass of dissolved metal during pit growth was obtained by integration of the chronocoulometry and applying Faraday’s law to get the mass of dissolved metal from the transferred electric charge. The potentiostatic method permitted the controlled growth of one up to three active pits. The electrochemical generation of pits was carried out using the same equipment, electrolytes and electrodes that were used in determination of the pitting potentials.

Natural pit nucleation and growth was induced in samples of both SS by immersion in 1.0 M ferric chloride solution at OCP conditions during the same periods of time as those for potentiostatic generation.

2.4 Pit profile measurement
The depth and morphology of the generated pits as a function of the anodic polarisation time was determined by means of a method of measuring material removal, using a metallographic microscope coupled to a digital camera with an image analysis system, and a Vickers HV-50A Hardness tester. The measurement of the metal thickness required for the complete removal of the deepest pit (the real pit depth) gave a variation of ±6 percent from repeated tests. The volume of metal dissolved from the generated pits was determined from data of material removal considering both hemispherical and semi-elliptical geometry and was compared with volume calculated from electrochemical data.

3. Results

3.1 Polarisation tests
Figure 2(a) and (b) shows the polarisation curves for both SS alloys tested in chloride containing electrolytes of different conductivity. The E_corr and E_p of 304L stainless steel in natural seawater were −180 ± 30 mV and 350 ± 40 mV vs SCE, respectively, and −250 ± 50 mV and 300 ± 40 mV in 3.5 wt.% NaCl solution. An average E_p value was used as the reference for the potentiostatic generation of pits in the steel.

From polarisation curves shown in Figure 2, the values ΔE = E_p − E_corr were determined for both SS as a function of the conductivity, as shown in Figure 3. This difference in the potential values was consistent for both SS as a function of electrolyte conductivity.

<table>
<thead>
<tr>
<th>Electrolyte: 3.5 wt.% NaCl solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
</tr>
<tr>
<td>AISI 316</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrolyte: natural seawater</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
</tr>
<tr>
<td>AISI 316</td>
</tr>
</tbody>
</table>

Table II Characteristics of the electrolytes used for electrochemical tests

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Concentration</th>
<th>Conductivity (mS cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl solution</td>
<td>0.001 M</td>
<td>0.121</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>0.01 M</td>
<td>1.172</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>0.1 M</td>
<td>10.51</td>
</tr>
<tr>
<td>FeCl₃ solution</td>
<td>0.05 M</td>
<td>15.55</td>
</tr>
<tr>
<td>Natural seawater</td>
<td></td>
<td>50.6</td>
</tr>
<tr>
<td>Sterilised/filtered</td>
<td>3.5 wt.%</td>
<td>55.8</td>
</tr>
<tr>
<td>NaCl solution</td>
<td>1 M</td>
<td>85.6</td>
</tr>
<tr>
<td>FeCl₃ solution</td>
<td>1 M</td>
<td>93.2</td>
</tr>
</tbody>
</table>

Figure 1 Schematic of the potentiostatic polarization sequence used for the generation of pits (potential in mV vs SCE)
3.2 Pits generated under potentiostatic control

The current generated by the anodic polarisation of the specimens for different time periods during the potentiostatic formation and growth of the pits was recorded as chronoamperometries. A minimum of four potentiostatic polarisations were carried out on different specimens under identical test conditions. Figure 4 shows the data of charge \( Q \) (in Coulomb, obtained from integration of the area underneath the chronoamperometries) for the AISI 304L and AISI 316 in natural seawater and 3.5 percent NaCl solution as a function of the polarisation time.

Figure 5 shows the quantity of dissolved metal (in \( \mu g \)) as a function of the time of anodic polarisation (in minutes) for the AISI 304L and AISI 316 steels in natural seawater and 3.5 wt.\% NaCl solution.

3.3 Volume determined from material removal

In the present study, pits generated under potentiostatic polarisation and at open circuit potential presented a hemispherical morphology. Figure 6 shows the tendency
3.4 Empirical pit growth law

The MPD as a function of polarisation time for the AISI 304L and AISI 316 steels in different electrolytes is shown in Figure 7. Pits generated under potentiostatic control presented a higher depth than did pits generated at open circuit potential in FeCl₃. Nevertheless, the pit depth variation as a function of time presented the same tendency. Pits generated in AISI 304L steel were deeper than were those generated in AISI 316 steel in the three electrolytes.

4. Discussion

4.1 Polarisation tests

The $E_{\text{corr}}$ and $E_p$ of 304L stainless steel changed to more active values as the conductivity of the electrolytes increased. The susceptibility of SS to suffer pitting corrosion can be evaluated through the difference $\Delta E = E_p - E_{\text{corr}}$. The results shown in Figure 3 indicate that the AISI 316 steel presents higher resistance to pitting corrosion than AISI 304L steel. A minimal effect of electrolyte conductivity on $\Delta E$ was observed in the conductivity range from 0.121 to 50.9 mS cm⁻¹.

4.2 Pits generated under potentiostatic control

Integration of the current vs time curves (chronoamperometries) obtained from the potentiostatic generation of pits gave the total charge generated due to pit growth. The total electric charge was divided by the number of pits that grew in an active way during the whole period of polarisation, obtaining in this way the electric charge per pit associated with the localised dissolution on both SS. From the electric charge the corresponding quantity of dissolved metal per pit was calculated using Faraday’s law. The calculations were carried out according to the chemical composition (wt.%) of the steels reported in Table I. The values of the quantity of dissolved material as a function of the anodic polarisation time were fitted using equation (1):

$$MD_{\text{CA}} = ct^d$$

where $MD_{\text{CA}}$ is the quantity of dissolved material per pit (in $\mu$g), $t$ is the time of anodic polarisation (in minutes) and $c$ and $d$ are constants. Zhou and Turnbull (1999) generated pits on 12 percent Cr martensitic stainless steel in 0.1M NaCl solution by applying the same electrochemical procedure used in the present study. From linear regression analysis, these authors reported a pit growth law that can be expressed by: $a = 48t^{0.53}$, where $a$ is the MPD in $\mu$m and $t$ is the time in minutes.

4.3 Volume determined from material removal

Newman and Franz (1984) reported values of pit growth under potentiostatic polarisation in S30400 stainless steel in 1M NaCl solution containing 0.04M Na₂S₂O₃. The generated pits exhibited a hemispherical morphology. These authors found good agreement between the results obtained via Faraday’s law and those obtained from measurements with an optical microscope. In the present case, the results shown in Figure 6 show that the volume of pits calculated considering hemispherical geometry (from material removal) matched better with the volume determined from chronoamperometry curves.

4.4 Empirical pit growth law

The empirical equation that best fit the experimental data of pit growth under potentiostatic control (in NaCl solution and in natural seawater) was plotted and is also shown in Figure 7 along with the curves from tests at OCP in FeCl₃. The power relationship between pit depth and polarisation time exhibited the form given by equation (2), as follows:

$$P_d = a - bt^c$$

where $P_d$ represents the pit depth in $\mu$m, and $t$ is the anodic polarisation time in minutes. Table IV presents the values of the constants obtained for equation (2) for both SS in the three different electrolytes.

Pits generated on S30400 and S31603 steels in artificial seawater applying the same electrochemical procedure used in the present study showed different empirical equations for the pit growth law (González-Sánchez, 2002). The behaviour is similar but the equation reported in that work was simpler. Specifically, for pits generated in the S31603 steel, the equation had the form described by equation (3):

$$P_d = 26t^{0.6}$$
and for S30400 steel, also in artificial seawater, the equation that represents the pit growth was:

\[ P_d = 27.9t^{0.67} \]  

(4)

where \( P_d \) is the MPD in \( \mu \text{m} \) and \( t \) is the polarisation time in minutes.

During the potentiostatically controlled pit growth it was observed with the aid of an optical microscope that in most of the cases only one pit grew actively. In some of the experiments however, two, or a maximum of three pits were detected growing actively. It has been suggested that metastable pit growth is established initially by the presence of a pit cover that helps to maintain the aggressive local chemistry within the pit (Laycock and Newman, 1997). This cover eventually will collapse and a pit must survive this experience in order to become stable.

5. Conclusions

5.1 Potentiodynamic experiments

Potentiodynamic polarisation tests, under stationary conditions, carried out in specimens of AISI 304L and AISI 316 SS in different electrolytes show that the corrosion potential (\( E_{corr} \)) and pitting potential (\( E_p \)), of both SS decreased as the electrolyte conductivity increased. The \( \Delta E \) values indicated that the 316 steel was less susceptible to pit corrosion that was the 304L steel. The susceptibility to pit corrosion of both SS increased notably as a function of conductivity for values higher than 50.9 mS cm\(^{-1}\).

5.2 Electrochemical generation of pits

Pits generated on AISI 304L steel were deeper than were those generated in AISI 316 steel in the three test electrolytes (3.5 wt.% NaCl solution, natural seawater and 1M FeCl\(_3\) solution). Pits generated under potentiostatic control and at open circuit potential in both SS had a hemispherical morphology, and were deeper than were those generated under potentiostatic control. An empiric law for pit growth determined under static conditions had the form of an exponential equation.

Electrochemical measurements of pit growth, in terms of the quantity of dissolved metal per pit, fitted well with measurements of the volumetric pit profile obtained from material removal results and optical microscopy observations for the studied SS in contact with chloride containing electrolytes.
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Figure 7 MPD as function of the potentiostatic polarisation time for (a) AISI 304L and (b) AISI 316 steels in electrolytes of different conductivity

Table IV Constant a, b and c values obtained for equation (2)

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrolyte</th>
<th>Conductivity (mS/cm)</th>
<th>Constant a</th>
<th>Constant b</th>
<th>Constant c</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304L</td>
<td>Natural seawater</td>
<td>50.6</td>
<td>852.996</td>
<td>782.721</td>
<td>0.987</td>
</tr>
<tr>
<td></td>
<td>3.5 wt.% NaCl solution</td>
<td>55.8</td>
<td>692.828</td>
<td>659.342</td>
<td>0.980</td>
</tr>
<tr>
<td></td>
<td>1 M FeCl₃ solution</td>
<td>93.2</td>
<td>378.943</td>
<td>347.104</td>
<td>0.972</td>
</tr>
<tr>
<td>AISI 316</td>
<td>Natural seawater</td>
<td>50.6</td>
<td>544.969</td>
<td>507.994</td>
<td>0.977</td>
</tr>
<tr>
<td></td>
<td>3.5 wt.% NaCl solution</td>
<td>55.8</td>
<td>461.483</td>
<td>401.621</td>
<td>0.972</td>
</tr>
<tr>
<td></td>
<td>1 M FeCl₃ solution</td>
<td>93.2</td>
<td>243.517</td>
<td>200.245</td>
<td>0.953</td>
</tr>
</tbody>
</table>

References


Corresponding author

L. Dzib-Pérez can be contacted at: luirdzib@uacam.mx