The Effect of Nitrate on Salt Layers in Pitting Corrosion of 304L Stainless Steel

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Current oscillations were observed during one-dimensional pitting corrosion of 304 L stainless steel in neutral 1 M NaCl solutions with varying NaNO3 concentrations. Synchrotron X-ray diffraction was used to identify the salt layer at the corrosion front. It was found that, although current oscillations were induced in solutions with higher concentrations of NaNO3, the salt species in the pit did not change and a nitrate-free salt was present in all solutions. At higher NaNO3 concentrations, a change of salt crystal morphology was detected. Electrochemical oscillations were seen to coincide with secondary pitting on the pit surface indicating that two corrosion regimes were operating in parallel. Synchrotron radiography was used on artificial pits to measure the change in corrosion front and material loss in situ. Before nitrate was added, the corrosion front showed non-uniform material loss across the interface when beneath the salt layer. Nitrate addition induced a local region of passivation that propagated across the pit surface. Surface roughness was quantified using R-values and seen to vary without a clear trend until passivation, after which it stayed constant. A mechanism is suggested in which partial passivation occurs in these systems, where passivated areas are undercut as the corrosion front moves, generating surges in current.

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Nitrates are known to be a powerful passivating agent for stainless steel.1,2 This has been attributed to enhanced passive film growth, with more rapid formation of a thinner film in nitrate solutions than in chloride solutions.3 Electrochemical polarization of stainless steel in a chloride solution with nitrate additions shows the existence of a passivation potential above which the current drops dramatically.4 This potential is strongly influenced by nitrate concentration, with higher concentrations leading to a lower passivation potential and a higher pitting potential.5,6

However, dilute concentrations of nitrate can have deleterious effects on corrosion behavior. It has been known for over 200 years that dilute concentrations of nitric acid can increase corrosion rate of Fe rather than reduce it.6,7 Oscillations in electrochemical behavior have been observed in chloride solutions with trace nitrate near the passivation potential.8–10 Nitrate additions to chloride solutions can also affect metastable pitting events in austenitic stainless steels, inhibiting slow-rise transients and causing localized inhibition.11

The exact mechanism of nitrate-induced passivation remains elusive. The presence of a “nitrate-rich salt layer” has been proposed,5 which may be a molten salt as suggested for dissolution of Fe in concentrated NaNO3 solutions.12 The correlation observed between the passivation potential and nitrate/chloride ratio4,11,13,14 has been attributed to competitive adsorption of nitrate and chloride ions.5

Nitrate reduction reactions have also been suggested as the cause of passivation since they may lead to increasing pH8–10. Electroreduction of NO3− to NH4+ has also been proposed15 but no evidence of reduced nitrogen species in solution has yet been found.16 The formation of bubbles on electrochemically-polarized carbon steel has been observed in nitrate/nitrite solutions, and these have been attributed to N2 formation from the reduction of nitrite ions.17

Artificial pit (“lead-in-pencil”) electrodes have frequently been used in electrochemical experiments to simplify the geometry and subsequent modelling of corrosion processes.18–21 When the rate of metal ion generation at the dissolution metal surface exceeds the rate of metal ion diffusion out of the pit, a salt layer can nucleate.22–25 The artificial pit electrode can be treated as a one-dimensional pit growing under diffusion control with the pit depth as the diffusion layer when it is deep enough for external diffusion from the pit mouth to be neglected.26 However, a salt layer can still form at shallower depths. Active dissolution under a salt layer is self-regulating: the thickness of the salt layer adjusts so that the potential drop across it leads to an interfacial potential across the metal/salt layer interface generates metal ions at the same rate as they diffuse away from the surface of the salt layer.19 However, it has recently been shown that microscopic roughness can develop under salt layers.27

Synchrotron X-ray diffraction has been used to characterize salt layers in artificial pits, which can be regarded as a slurry of crystallites settling.25,27,28 Recent XRD work on Fe foils in HCl solution containing trace amounts of nitrate27,28 has shown the presence only of FeCl2·4H2O salt species, but with anisotropy in the salt layers in the presence of nitrate. Solutions of 0.1 M HNO3 with trace chloride gave rise to Fe(NO3)2·6H2O salt species, also with anisotropy. In this work, synchrotron X-ray diffraction and electrochemical methods are used on artificial pits to show the creation of salt layers and identify the layers present when oscillatory current behavior is seen in a dilute NaNO3/NaCl electrolyte on stainless steel. Synchrotron radiography is also used to track material loss in situ and give insight to the passivation behavior in the pits.

Experimental

Diffraction.— Samples were prepared following the method described by Rayment et al.23 Working electrodes were constructed from 3 mm wide strips of 30 µm thick 304 L stainless steel (18 wt% Cr, 10 wt% Ni) (Goodfellow) as shown in Figure 1. These were embedded in Araldite epoxy resin (3M). The active end of the electrode was attached to a reservoir by Kapton tape (3M). The reservoir was filled with 20 ml of 1 M NaCl containing an Ag/AgCl reference electrode and a Pt counter electrode (All potentials are quoted on the Ag/AgCl scale). The working electrode was then corroded electrochemically for 6 hours with a potential of 1 V to produce a pit of approximately 1 mm depth. The voltage was controlled using an Ivium Compactstat potentiostat.

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Diffraction experiments were conducted in situ on using the microfocus spectroscopy beamline I18 at the Diamond Light Source,\textsuperscript{29} using an X-ray beam spot size of 2.5 μm (h) × 20 μm (w) and a beam energy of 12.00 keV. A CCD detector was used with a resolution pixel size of 26 μm × 26 μm. To reduce beam damage\textsuperscript{30} a 0.75 mm Al-foil was used to reduce the intensity of the incoming beam and diffraction exposure time was limited to 15 seconds. At the start of each scan, the sample was positioned such that the X-ray beam was above the dissolving electrode and its salt layer. The sample was held for 600 s at each potential until passivation was observed.

The salt layer was characterized in 1 M NaCl solution at a range of potentials, from 0.3 V to 0.7 V, as summarized in Table I. The cell solution composition was then changed to 40 mM NaNO$_3$/1 M NaCl, 50 mM NaNO$_3$/1 M NaCl, then finally up to 75 mM NaNO$_3$/1 M NaCl at the potentials shown in Table I. Current was observed during each experiment to ensure the pit did not passivate.

### Electrochemistry

The results from potential cycling are shown in Figure 3. The pit was initially grown in 1 M NaCl at 1 V and then maintained at a potential of 1.2 V to reach a diffusion-controlled steady state with a salt layer on the dissolving surface. Figure 3a shows a potentiodynamic cycle starting from point A at a sweep rate of 2 mV s$^{-1}$. As the voltage decreases, the current maintains a steady level due to the diffusion limited conditions. As the potential decreases further, the salt layer thins until at point B it has completely dissolved. Between points B and C the salt-free surface is undergoing dissolution under mixed activation/ohmic control. On the reverse sweep, between

![Diagram](image-url)
Figure 3. (a) Current in 304L artificial pit when potential is swept from 1.2 V to −0.1 V, then back. Sweep rate 2 mV/s. Solution is 1 M NaCl. (b) Potential sweep made again when solution is changed to 1 M NaCl/75 mM NaNO3. Letters on the figures are discussed in the accompanying text.

C and D, the current has reached significantly higher levels due to the absence of the salt layer. At point D, the solution is sufficiently supersaturated for a new salt layer to precipitate. The supersaturated salt precipitates out of solution creating an extra thick salt layer which provides a particularly high \( IR \) drop (e.g. 35). This causes a transient drop in the current (E), which is rapidly restored to the diffusion-controlled steady state value which is maintained up to 1.2 V (F).

At the end of the experiment shown in Figure 3a, the solution was changed to 75 mM NaNO3/1 M NaCl and mixed by pumping the solution several times with a syringe. The electrochemical behavior of the pit shown in Figure 3b is similar to that of 1 M NaCl solution until a potential of 0.5 V (Ag/AgCl) was reached on the reverse sweep (see point G on Figure 3b). At this potential, the current dropped to almost zero. These data are consistent with Figure 4 in Newman and Ajjawi8 for the same ratio of \( \text{NO}_3^-/\text{Cl}^- \).

Figure 4 shows a series of potentiostatic experiments in which the potential was stepped from 0.3 V to 0.5 V in the solution of 75 mM NaNO3/1 M NaCl. Figure 4a shows that the current quickly peaks and drops due to the precipitation of a salt layer from supersaturated solution and thus levels out to a stable limiting current of approximately 0.08 mA. At 0.4 V (Figure 4b), the initial trend matches that seen at 0.3 V and maintains a stable current after a salt layer is precipitated out and thins to a stable level at approximately 0.08 mA. After 400 s mild perturbations occur in the current. At 0.5 V (Figure 4c), large current oscillations occur immediately after the salt layer has formed. The magnitude of these oscillations occurs in the region around the limiting current. The oscillations are stable in the cell, continuing in excess of 1200 s and have a period of between 80–100 s.

The oscillations seen in 75 mM NaNO3/1 M NaCl were reproduced under laboratory conditions and the pit surface was subsequently imaged using SEM. When the pit was grown in 1 M NaCl for 4 hours at 1 V, the pit surface appears roughened but generally evenly corroded (Figure 5a). In an experiment with a solution of 75 mM NaNO3/1 M NaCl, electrochemical oscillations similar to those shown in Figure 4c were observed. Under these conditions the pit surface showed extensive secondary pitting (Figure 5b).

X-ray diffraction.—Diffraction patterns from the salt layers taken during these experiments are shown in Figure 6a. The same diffraction pattern was seen in nitrate-free solutions as in those with higher nitrate concentrations. This pattern looks similar to FeCl2.4H2O described by Verbist et al.,36 except that several minor peaks are missing from the data, indicating a change in space group, symmetry, or preferential orientation. In the presence of nitrate no other significant phase is observed. Austenite peaks from the base metal are also seen in both figures.

In 75 mM NaNO3/1 M NaCl solution, the same diffraction pattern is found at high applied potential when current oscillations are being observed as at low applied voltage, indicating that there is no change in salt species during these oscillations (Figure 6b).
Figure 5. SEM images of corrosion surface of one-dimensional pits when (a) grown for 4 hours in 1 M NaCl at 1 V with no current oscillation was observed, and (b) grown for 4 hours in 1 M NaCl at 1 V, then 4 hours in 1 M NaCl/75 mM NaNO₃ at 0.5 V with current oscillations observed.

Figure 6. Diffraction patterns of salt layer collected in one-dimensional pits of 304L (a) in 1 M NaCl at 0.5 V with varying NaNO₃ concentration, and (b) in 1 M NaCl/75 mM NaNO₃ with varying applied voltages. Diffraction pattern for FeCl₂·4H₂O is also shown.

Figure 7. (a) Salt layer XRD pattern at 0.5 V in 1 M NaCl with stable limiting current and (b) at 0.5 V in 1 M NaCl/75 mM NaNO₃ generating oscillating current. Electrochemical data shown in Figure 4.

From Figure 5b it is clear that the dimensions of the secondary pits are much smaller than the thickness of the foil. As such, diffraction patterns collected would be summed across the thickness, so it would be difficult to detect distinct phases within the secondary pits. This is also true with the electrochemical data. Although the species of salt appears to be uninfluenced by nitrate concentration, the intensity and spread of points on the 2-D diffraction patterns did change. In pure chloride solutions the diffraction rings show anisotropic behavior (Figure 7a). For example the (002) reflection is strongest at the top and bottom of the ring, whereas the (100) reflection (which is crystallographically perpendicular to (002)) diffracts predominantly to left and right, indicating the presence of preferential orientation. This would be consistent with plate-like crystallites settling with the (002) planes horizontal. When nitrate is added, the anisotropy becomes reduced, but close examination reveals that the rings show more distinct spots (particularly the (120) reflection), suggesting that the crystallites may be larger (Figure 7b).

Radiography.— Results from radiography experiments are shown in Figure 8, with solution initially being 1 M NaCl and changed to 75 mM NaNO₃/1 M NaCl at approximately 500 s. The current (Figure 8a) wasn’t affected until 775 seconds, where it is seen to drop dramatically. The corrosion front is distinguishable from radiographs (Figure 8b) via the use of an edge-detection processing. This showed...
material loss in 100 second intervals over the period from 0 to 1400 s (Figure 8c). Up until 800 s the rate of dissolution is fairly consistent across the interface, but local variations in the rate of material loss can be observed. After 800 s, the radiograph edges begin to overlay each other (except for the right hand end of the foil) indicating a predominantly fixed interface and no material loss. This coincides with a significant drop in current. The surges of current that occur after most of the foil has passivated (Figure 8d) coincide with bursts of dissolution that occur at a creviced site on the right hand side of the foil (Figure 8c). The elevated current at the end of the passive region in Figure 3b might also be a result of such a crevice. The voltage was held at 0.4 V until 1800 s, then increased to 0.45 V until 2400 s, then increased to 0.5 V where the cell passivated. These bursts continued until passivation. This passivation potential was lower than that recorded during the diffraction experiments (0.6 V), which had a thicker foil cross-section (50 μm).

**Corrosion front roughness.**—An attempt to interpret surface roughness was made using standard quantification techniques. An attempt to interpret surface roughness was made using standard quantification techniques. The mid-region of the foil interface was extracted then a background was calculated by averaging the values of 50 pixels either side of each point horizontally (101 points in total) as this size was larger than local features on the interface so would not remove them when subtracted (Figure 9a). This moving average background was subtracted from the original interface scan, normalising the data and allowing R-values to be calculated for each scan.

Surface roughness was quantified using Root Mean Square standard deviation:

$$ R_{SD} = \sqrt{\frac{1}{M} \sum_{j} (R_j - R_a)^2} $$

Where $M$ is number of points, $R_j$ is height at point $j$, and $R_a$ is average height. It is shown that while corrosion is proceeding along the foil the roughness $R$-value varies in a non-linear fashion (Figure 9b). Once passivation begins at 800 s roughness becomes more pronounced, and after passivation roughness remained constant and larger than when corroding.

Figure 10a shows the background-corrected scans of the foil, calculated in Figure 9a, plotted against time. Peak and trough positions in the roughness of the foil drift along the surface until passivation occurs where these become fixed in position and height. To investigate rates of dissolution, values of the original scan interface were subtracted vertically at 10 s intervals to see the variation in the rate of change over the foil (Figure 10b). Initially the entire interface had a negative change (dy/dt), i.e. the entire interface was corroding, but with
when nitrate was added in similar experiments with Fe. This can be explained by a change in space group, symmetry, or by preferred orientation, as noted above. While the observed crystal structure for the iron II chloride layer formed during rapid dissolution of stainless steel has yet to be satisfactorily modelled, it is clear that the same salt species occurs whether or not current oscillations are observed, in both nitrate-free and nitrate-rich solutions. It therefore follows that the salt crystal structure does not contain a significant concentration of nitrate ions. This does not necessarily contradict previous discussions of a nitrate-rich salt layer as the formation of the iron chloride salt layer may instead concentrate nitrate into the solution surrounding the salt crystallites.

The salt layer on the pit surface is dynamic, and can be regarded as a slurry that has settled upon the dissolving surface. Anisotropy is likely to be a result of settling of, for example, plate-like crystals rather than as a solid layer with an epitaxial relationship with the substrate. The formation of plate-like crystals is likely to be associated with preferential adsorption of nitrate upon specific crystal planes. It is curious that in the case of stainless steel, anisotropy in pure chloride solution is lost on addition of nitrate to the solution, whereas in the case of pure Fe, isotropic diffraction is observed in pure chloride solutions and the addition of nitrate leads to anisotropic diffraction. This is not yet understood, but one could speculate that the likely culprit is chromium.

The secondary pitting seen on the pit surface is evidence of two corrosion regimes in operation. Under conditions close to the passivation potential, local variations in interfacial potential caused by an inhomogeneous salt layer may lead to localized patches of passivation on the pit surface. This concept is consistent with the radiography evidence, which shows regions of localized attack undercutting passivated regions. The passivated regions are sufficiently stable that localized crevicing is needed to activate the pit’s surface.

The observed passivation potential is lower in the radiography experiments than in the diffraction experiments. This may be associated with radiolytic effects but it should be noted that the thickness of the foils used for radiography foils was only 25 μm as compared with the diffraction foils which were 50 μm thick. There may be an effect associated with the size scale of passivated patches on the electrode. At 0.4 V, the 50 μm foil in the diffusion experiment shows small amounts of current irregularities whereas in the 25 μm radiography foils these variations are much greater. In the thinner foils, the passivated regions may butt up directly to the pit walls, leaving no active region around the passivated area to allow undercutting. Thus, there would be less attack around these regions and passivation is more easily achieved in thinner dimensions.

Radiography (Figure 10a) shows that, even in the absence of nitrate, the roughness varies significantly during corrosion under a salt layer, with peaks becoming troughs and vice versa. An SEM image of a typical surface is shown in Figure 5a. This is a consequence of variations in local current density, and continues following addition of nitrate. However, once the passivation process begins, the R-values of roughness are seen to increase markedly. This increased roughness is due to the loss of salt layer next to passive regions. When a region of the surface passivates, metal ions are no longer produced and continue to diffuse away from the surface, so the local metal ion concentration decreases. In these highly concentrated solutions, a decrease in concentration leads to an increase in both conductivity and diffusivity. The higher local conductivity of the solution at the edge of a passive region thus leads to a correspondingly higher local interfacial potential, and a higher local rate of dissolution. Figure 11 illustrates how such a process might lead to electrochemical oscillations associated with the secondary pits shown in Figure 5b. The salt-covered active surface before oscillation has a fairly uniform corrosion front (Figure 11a). Local passivation will reduce the total current, but highly active regions develop next to the passive region (Figure 11b). As the active surface continues to corrode, it can undercut the passive surface (Figure 11c) leading to its detachment, with an associated local surge in current (Figure 11d). This surge will cause local supersaturation of the metal ions, bringing the current down again. It is proposed that
Figure 11. Possible mechanism of oscillation in current – (a) Normal corrosion front before oscillation, (b) localized passivation blocks some of the corrosion front, but allows limited dissolution to continue, (c) This continued localized dissolution undercuts passivated regions, (d) these undercut regions are ejected, allowing newly active region to surge in corrosion.

The pits shown in the SEM images in Figure 5b are a consequence of such a local dissolution process.

Alternative explanations tend to treat oscillatory behavior as a homogeneous process taking place uniformly over the entire surface, for example, in Fe systems, it has been proposed that the electric field across the salt layer drives H$^+$ into the bulk solution, raising the local pH and passivating the local interface. This in turn reduces the corrosion rate, allowing the repelled H$^+$ to be attracted to the surface again, increasing the corrosion rate. This mechanism is less convincing in these experiments because it does not account for the localized attack shown in Figure 5b.

The propagation of passivation seen in the radiography experiment can be considered using a similar mechanism. If the local passivated region is large, the overall loss in generation of metal ions may be insufficient to maintain a sufficiently concentrated solution to sustain active dissolution, allowing the passive region to propagate across the surface.

Since salt crystals are insulators, all of the current is carried in the solution along channels between them. This leads to an inherent inhomogeneity in local dissolution. As the crystallites coarsen with addition of nitrate (Figure 7), the scale of the local heterogeneity is likely to become greater, increasing the possibility of local inhomogeneous attack with associated oscillatory behavior.

Conclusions

For 304 L stainless steel artificial pits in NaCl /NaNO$_3$ solutions, dissolution under a salt layer takes place up to a critical potential where passivation takes place. Just below this passivation potential, current oscillations have been observed.

The crystal structure of the salt layer was the same regardless of nitrate concentration or whether current oscillations were observed, indicating that nitrate is not incorporated in the crystalline phase formed in the salt layer. The diffraction pattern approximately matches FeCl$_3$.4H$_2$O as described by Verbist et al. with some minor peaks missing.

In diffraction patterns from the salt layer, a decrease in anisotropy was observed with increasing nitrate concentration, indicating that there is a change of salt crystal morphology, possibly a result of formation of platelets that settle parallel to the metal surface. This trend is the opposite of that previously found with nitrate additions to Fe in HCl solutions.

Ex situ SEM images showed that secondary pitting had occurred under conditions where current oscillations were observed. Radiography also shows both active and passive regions existing at conditions near passivation. This indicates a partial passivation process occurring on the surface of the pit. It is proposed that this allows undercutting of passive regions, resulting in oscillatory behavior.

Radiography data were taken simultaneously while collecting electrochemical data. Roughness was observed during dissolution before nitrate addition, indicating the presence of heterogeneity in localized current density. The peaks and troughs of the roughness changed position during dissolution. Once partial passivation was observed, it propagated across the corrosion surface. After passivation, the roughness stayed constant, with corrosion instead progressing in a localized crevice at the foil edge.

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References

1. H. H. Uhlig and J. R. Gilman, *Corrosion*, 20, T289 (1964).
2. M. A. Rodriguez, *Corrosion Reviews*, 30, 19 (2012).
