Inhibitive Effect of Nitrate on Pitting Corrosion of 17-4PH Stainless Steel

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ABSTRACT

In this work, the inhibition effect of nitrate on the pitting corrosion of 17-4PH stainless steel was investigated in the chloride solution. Potentiodynamic and potentiostatic techniques were used to measure the pitting potential and induction time in various concentrations of chloride and nitrate ions. According to the results, the equation of \( E_{\text{pit}} = 259.1 - 147.4 \log(\text{Cl}^-) + 52.1 \log(\text{NO}_3^-) \) was developed to show the relationship between the pitting potential and the concentrations of nitrate and chloride ions at room temperature. Moreover, it has been shown when the ratio of \( \frac{\text{NO}_3^-}{\text{Cl}^-} \) is greater than a threshold value of 0.35, the alloy remains passive in whole potentials during the potentiodynamic experiments. In addition, the results indicated that pitting is rarely observed in the potentials above the 400 mV\(_{\text{SCE}}\) in the chloride solutions containing nitrate.

KEY WORDS: 17-4PH steel, chloride, inhibitor, nitrate, pitting corrosion

INTRODUCTION

17-4PH stainless steel (UNS S17400\(^{(1)}\)), known as a precipitation hardening martensitic stainless steel, has found extensive applications because of its attractive combination of appropriate corrosion resistance and good mechanical properties. This type of steel is widely used in many applications including aerospace industry,\(^{1}\) steam turbine shafts and blades, and nuclear industry.\(^{2-5}\) Heat treatment of 17-4PH stainless steels includes a solution annealing and cooling to obtain a martensitic structure, followed by aging treatment which leads to the formation of Cu-rich precipitates.\(^{6}\)

Aging temperature for this stainless steel varies from 480°C to 620°C. By aging at 480°C for 1 h, the mechanical resistance of the steel is improved.\(^{3}\) The corrosion resistivity of the stainless steel is a result of the formation of oxide film on the steel’s surface, which is compact and adherent in nature. In the aqueous medium, this passive film consists of two layers, including a chromium-rich inner barrier oxide layer and iron-rich outer deposited hydroxide layer.\(^{7-13}\) However, in the presence of aggressive ions like chlorides, this passive film is often vulnerable to localized breakdown on the defect sites, leading to localized corrosion such as pitting corrosion. The aggressiveness of chloride is a result of its high diffusivity, strong anionic nature, and high solubility.\(^{12-14}\)

It has been shown that pitting potential of a metal has a linear relationship with the logarithm of the aggressive anion concentration. This relationship is described by the following equation:

\[
E_{\text{pit}} = A - B \log C_{\text{agg}}
\]
where A and B are constants, $E_{\text{pit}}$ is the pitting potential, and $C_{\text{agg}}$ is the concentration of the aggressive anion in mol/L.\textsuperscript{15} As expected, the higher aggressive anion concentration leads to lower pitting potential.

Various attempts have been made to prevent or control the damaging effect of corrosion on stainless steels in chloride solution. The use of corrosion inhibitors is one of the most effective prevention methods. Two types of corrosion inhibitors have been extensively used to protect metals from corrosion, including adsorption inhibitors and metal passivation inhibitors.\textsuperscript{16} The use of nitrate, which is a passivating inhibitor, is a promising alternative for preventing metal dissolution in chloride-containing media.\textsuperscript{17-18} According to Leckie and Uhlig,\textsuperscript{19} pitting inhibition efficiency of the nitrate anions on austenitic stainless steels is higher than perchlorate and sulfate anions, but lower than hydroxide anion in chloride solution with concentrations higher than 0.1 M.

Schwenk\textsuperscript{20} reported that nitrate ions inhibited pitting of the stainless steel in chloride-containing solutions, whereas this ion did not inhibit pitting corrosion in bromide-containing solutions. In stainless steels, the beginning of pitting corrosion in aqueous solutions mostly shifts to higher potentials as the concentration of the inhibitor increases.\textsuperscript{19,21-25}

A logarithmic relationship between the pitting potential, $E_{\text{pit}}$, and the ratio of the inhibitor to the aggressive ion concentration is reported as follows:\textsuperscript{26-27}

$$E_{\text{pit}} = K + \log \left( \frac{[\text{C}_{\text{inh}}]}{[\text{C}_{\text{agg}}]} \right)$$

where $K$ and $n$ are constant, $E_{\text{pit}}$ is pitting potential, and $C_{\text{inh}}$ and $C_{\text{agg}}$ are concentrations of inhibitive and aggressive ions, respectively.

The following relationship has been described to propose the threshold concentration of inhibitive ions, $C_{\text{inh}}$, in the solution containing chloride with concentration of $C_{\text{agg}}$:

$$\log C_{\text{inh}} = P + Q \log C_{\text{agg}}$$

where $P$ and $Q$ are constant and $C_{\text{inh}}$ is the threshold concentration of the inhibitive ions in the solution containing chloride with concentration of $C_{\text{agg}}$.\textsuperscript{28}

According to the Uhlig and Gilman,\textsuperscript{29} nitrate ions shift the pitting potential to the more positive values, although it is contended that nitrate does not affect the pitting corrosion simply.\textsuperscript{20} Clearly, inhibition effect of nitrate ions on the pitting corrosion has not been understood very well. It is believed that nitrate inhibits pitting corrosion by forming a passive film on the specimen surface, which protects it against aggressive ions and consequently increases the pitting potential.\textsuperscript{17-18}

Pitting corrosion inhibition by nitrate ions probably involves several mechanisms:\textsuperscript{19,30}

(a) competitive adsorption between nitrate and chloride anions because of the same mobility and electron charge, (b) redox reactions between Fe$^{2+}$ and nitrate ion, which consumes acid (depending on the pH) or produces a barrier layer of Fe(OH)$_3$, and (c) electro-reduction of the nitrate ions, which consumes acid. Newman and Ajjawi\textsuperscript{18} showed that nitrate is only able to passivate salt-covered pit surfaces, and this passivation only occurs over a critical potential. In the presence of the salt cover, not only does this cover behave as an ohmic conductor, but also previously mentioned mechanisms for nitrate inhibition occur faster at the interface of the salt and the solution. Pitting corrosion of bulk specimen of 18Cr-13Ni-1Nb stainless steel in pit-like solution based on either FeCl$_2$ or FeCl$_3$, and containing chromium and nickel chlorides in stoichiometric proportion as a function of increasing nitrate concentration, was investigated by Whillock, et al.\textsuperscript{31}

In intermediate nitrate concentration, an increase in apparent current density was observed in both solutions and no threshold nitrate to chloride concentration for transition from pitting to passivation was reported. When they used a wire electrode, a passivation under the salt was observed at a threshold NO$_3$/$Cl^-$ molar ratio of 1 to 5.

Research conducted by Newman and Ajjawi\textsuperscript{18} has shown that nitrate can strongly inhibit pitting corrosion of Type 304 stainless steel (UNS S30400) in chloride solutions. Using a wire electrode, they reported that if the nitrate concentration is less than a critical amount, stable pitting will happen.\textsuperscript{19} However, above this critical concentration, the inhibitor ions eliminate pitting corrosion occurrence.\textsuperscript{19,26,29} Local pit repassivation under the salt in solution consisting of nitrate and chloride ions was reported by Street, et al.\textsuperscript{32} Using synchrotron $x$-ray diffraction in conjunction with the polarization of a pencil electrode made of Type 304 stainless steel, they reported that nitrate addition induces a local region of passivation that propagated across the pit surface and also morphology changes of salt layer at higher concentration of nitrate solution.

In this research, the effect of nitrate inhibition on the pitting corrosion of 17-4PH stainless steel in chloride solution is investigated. Electrochemical techniques were used to establish a relationship between the pitting potential and the inhibitive and aggressive ion concentrations. Based on the results, the values of key constants in a well-known equation for the variation of the pitting potential as a function of aggressive and inhibiting ion concentrations are developed. Moreover, in this research, with the help of potentiotodynamic experiments, a threshold ratio of nitrate to chloride concentration is estimated, above which pitting would not occur.
EXPERIMENTAL PROCEDURES

Sample Preparation
The chemical composition of 17-4PH martensitic stainless steel used in this study is given in Table 1. Specimens were cut in cubic shape with dimensions of 1 cm x 1 cm x 0.5 cm. At first, all of the specimens were solution annealed for 1 h at 1,050°C and then tempered at 480°C for 1 h. In order to avoid crevice corrosion at the interface of the sample and polymeric mount, the specimen was exposed to 0.1 M Na2SO4 solution at the anodic potential of 850 mVSCE for 900 s to form the passive film on the surface prior to mounting. Working electrodes, with 1 cm² exposed area, were made by mounting with a self-cure epoxy resin. Electrical connection was made by connecting a copper wire to back of the specimen. Before each electrochemical experiment, working electrodes were prepared by surface abrading with the silicon carbide (SiC) emery papers from 60 to 1200 grade, rinsing with distilled water, degreasing with ethanol, and finally drying with warm air.

Electrochemical Measurements
All electrochemical measurements were performed with a Gill AC† automated potentiostat (ACM instruments) controlled by a computer. All solutions were prepared with distilled water and analytical reagents of sodium chloride and sodium nitrate. The electrochemical experiments were performed in an open 250 mL beaker filled with 100 mL of solution. Electrochemical cells were performed by a conventional three-electrode cell, which is composed of a working electrode, a platinum sheet as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. All of the tests were performed at room temperature (20±2°C) and all potentials are referenced to the SCE.

The measurement techniques used in this study were potentiodynamic and potentiostatic polarization tests. In order to reach a steady state condition, open-circuit potential (OCP) of the working electrode was measured for 3,600 s and 900 s before potentiodynamic and potentiostatic tests, respectively.

Potentiodynamic Polarization Techniques — Pitting corrosion of the samples and the effect of the chloride concentration on the pitting potential was investigated using potentiodynamic polarization techniques in 0.0025, 0.025, 0.25, 0.5, and 2.5 M sodium chloride solutions. In order to investigate the inhibitive effect of nitrate, different concentrations of sodium nitrate (0.0005, 0.005, 0.025, 0.05, 0.1, 0.12, 0.15, and 0.5 M) were added to the solution with various chloride concentrations.

In the potentiodynamic polarization method, experiments were performed by sweeping the potential from 50 mV below the OCP until the pitting corrosion occurred. Potentiodynamic scan rate of 30 mV/min was utilized. Pitting potential was considered the potential at which a sharp and sudden increase of the current density occurred without any repassivation. Because of the stochastic nature of the pitting corrosion, pitting potentials were measured by at least five repetitions in all experiments and the mean value was reported. To ensure the reproducibility of the pitting potential, some experiments were repeated 20 times and the results were depicted in the cumulative diagrams. The diagram indicates the pitting probability, P(E), as a function of potential, which is expressed as:

\[
P(E) = \frac{n}{1 + N}
\]  

where N is the total number of the repeated experiments, and n is the order number of samples which are assigned after sorting according to their pitting potential.

Potentiostatic Polarization Technique — Potentiostatic polarization experiments were performed at anodic potential of 100 mV SCE (50 mV below the pitting potential in 0.5 M NaCl) and 200 mV SCE (50 mV above the pitting potential in 0.5 M NaCl) in the solution containing 0.5 M NaCl and 0.5 M NaCl + 0.05 M NaNO3. Each experiment was repeated 25 times. The survival probability diagram is plotted according to the following equation:

\[
\text{Survival Probability} (%) = 1 - \left(\frac{n}{N + 1}\right) \times 100
\]

where N is the total number of the repeated experiments, and n is the order number of samples which are assigned after sorting according to their induction time.33

Microstructural Studies
Microstructural studies were conducted with the scanning electron microscope (SEM) model LEO VP 1450† to characterize the pit morphologies. For this

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*Hypertext Markup Language (HTML) and Extensible Markup Language (XML) content has been removed to ensure the natural text is presented accurately.*

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<td>0.012</td>
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</table>

† Trade name.

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TABLE 1
Chemical Composition of 17-4PH Stainless Steel Used in this Study
purpose, samples were first cleaned in an ultrasonic bath containing ethanol for 25 min. Then, the pit morphologies of both the nitrate-containing and free-nitrate solutions were characterized before and after ultrasonic preparation.

RESULTS AND DISCUSSION

Effect of Chloride and Nitrate on the Pitting Corrosion

It is well known that the pitting potential of the stainless steels is significantly affected by the chloride concentration. Chloride ions deteriorate the passivity and consequently decrease pitting potential to lower values. Figure 1 shows typical potentiodynamic polarization curves for 17-4PH stainless steel in solutions with different chloride and nitrate concentration. As illustrated in Figure 1(a), both corrosion and pitting potential reduce with increasing chloride concentration; however, passive current density increases. This behavior is known to be related to the aggressive nature of the chloride ions.

Studies on the nitrate effects on pitting behavior of the stainless steels show that adding nitrate to the chloride solution increases the pitting potential as a result of its inhibiting nature. The inhibitive effect of nitrate addition is shown in Figure 1(b). As indicated, further increasing in the nitrate concentration to a threshold ratio can eliminate the pitting corrosion entirely.

Potentiodynamic polarization curve in Figure 1(b) shows a hump-like region at about 400 mV SCE, which indicates a slight increase of the current that then returns to the passive plateau at approximately 600 mV SCE. The reason for this increase and decrease of the current density is not completely clear. A similar hump feature of the passive current density in potentiodynamic polarization curves of stainless steel was reported by Leckie and Uhlig and Lillard, et al., and they referred the potential at the end of the hump to the inhibition potential. At the potentials of the hump region, many fluctuations can be observed, especially in solution with lower nitrate contents. These fluctuations of the current density may be a result of the metastable pitting occurrence, which decreases with increases in the concentration of the nitrate ion. It means that nitrate addition may repassivate the metastable pits and inhibit their propagation. Similar results were reported by Lillard, et al., as the nitrate concentration increases, a decrease in metastable pitting activity and a shift to positive value of pitting potential was observed.

Pitting probability, P(E), of the steel in different concentrations of chloride and nitrate is depicted in the cumulative diagrams (Figure 2). These graphs show that pitting potential definitely increases with decreasing chloride and increasing nitrate content. Moreover, it can be seen that pitting potential distributions are relatively fine.

Furthermore, the pit survival probabilities were studied in an applied anodic constant potential to investigate how nitrate ions are able to inhibit stable pit formation. Figure 3 shows the survival probability plots, which indicate the induction time to form a stable pit at two different potentials, 100 mV SCE and 200 mV SCE in 0.5 M NaCl solution in presence and absence of 0.05 M nitrate. It is obvious that the survival probability for pitting of metal in a nitrate-containing solution is significantly higher than the solution without it. For example, after 1,000 s at 100 mV SCE, the survival probability in nitrate-containing solution is about 70%, and in chloride solution is approximately 30%. This fact demonstrates the inhibitive effect of nitrate ions that hinders the
transition of metastable to stable pitting. Moreover, the induction time of pitting decreases by increasing the applied potential.

**Safety Threshold for Pitting**

It is well known that the pitting potential is influenced by the chloride and nitrate concentrations, as described in Equation (2). According to this equation and pitting potentials obtained by the potentiodynamic experiments in solution containing various amounts of chloride and nitrate, development of a relationship between nitrate to chloride concentration ratio and pitting potential is attempted.

Figure 4 shows the results of the breakdown potential versus chloride concentration in solutions containing constant nitrate ion. Each point in the diagram represents the mean breakdown potential obtained from five experiments. As can be seen,
by increasing chloride concentration, the breakdown potential suddenly falls to the pitting values because of the aggressive effect of chloride on the passive layer. After that, the pitting potential decreases linearly by increases in chloride content. The mean value of the slopes of the linear part of the graph is calculated to be about $-150.6 \text{ mV/decade}$. The intercept values and $R^2$ (determination coefficient with linear regression) of the fitted lines with the slope of $-150.6 \text{ mV/decade}$ for solutions containing various concentrations of nitrate are listed in Table 2, to which the corresponding mean value of slope is defined as:

$$A = C + E \log[\text{NO}_3^-]$$  \hspace{1cm} (7)

C, D, and E in Equations (7) and (8) can be calculated by plotting the A and $A'$ values versus the logarithm of nitrate and chloride concentrations, respectively. Plots are demonstrated in Figure 6, which show a linear relationship between the intercept values and the logarithm of concentration. The results led to the values of 268.9 and 57.1 for C and E, respectively (Figure 6[a]). Likewise, values of 249.3 and 144.1 were obtained for C and D by plotting of $A'$ values versus logarithm of [Cl$^-$. Figure 6[b]].

From the results of solutions with constant nitrate, the following equation is obtained:

$$E_{pit} = 268.9 - 150.6 \log[\text{Cl}^-] + 57.1 \log[\text{NO}_3^-]$$  \hspace{1cm} (9)

The intercept values of the linear fittings are listed in Table 3, to which the corresponding mean slope is about 47.1 mV/decade. Moreover, it is obvious in Figure 5 that after a threshold value, the breakdown potential climbs suddenly from pitting potential to transpassivity potential. This fact means that pitting does not occur after a critical concentration ratio of nitrate to chloride, even at elevated potentials.

Therefore, the equations of $E_{pit} = A - 150.6 \log[\text{Cl}^-]$ and $E_{pit} = A' + 47.1 \log[\text{NO}_3^-]$ are obtained from the linear part of diagrams indicated in Figures 4 and 5, respectively. The obtained intercept values of A and $A'$ are presented in Tables 2 and 3. According to Equation (2), dependency of pitting potential to the nitrate and chloride ions concentration can be rewritten in form of:

$$E_{pit} = -D \log[\text{Cl}^-] + E \log[\text{NO}_3^-]$$  \hspace{1cm} (6)

Therefore, the value of A and $A'$ are defined as:

$$A = C + E \log[\text{NO}_3^-]$$  \hspace{1cm} (7)

$$A' = C - D \log[\text{Cl}^-]$$  \hspace{1cm} (8)

C. D, and E in Equations (7) and (8) can be calculated by plotting the A and $A'$ values versus the logarithm of nitrate and chloride concentrations, respectively. Plots are demonstrated in Figure 6, which show a linear relationship between the intercept values and the logarithm of concentration. The results led to the values of 268.9 and 57.1 for C and E, respectively (Figure 6[a]). Likewise, values of 249.3 and 144.1 were obtained for C and D by plotting of $A'$ values versus logarithm of [Cl$^-$] (Figure 6[b]).

From the results of solutions with constant nitrate, the following equation is obtained:

$$E_{pit} = 268.9 - 150.6 \log[\text{Cl}^-] + 57.1 \log[\text{NO}_3^-]$$  \hspace{1cm} (9)
and the results of solutions with constant chloride, led to the following equation:

$$E_{\text{pit}} = 249.3 - 144.1 \log[\text{Cl}^-] + 47.1 \log[\text{NO}_3^-]$$ (10)

Therefore, by averaging the above equations, an overall equation can be obtained to estimate the pitting potential as a function of chloride and nitrate concentrations. This equation could be written as follows:

$$E_{\text{pit}} = 259.1 - 147.4 \log[\text{Cl}^-] + 52.1 \log[\text{NO}_3^-]$$ (11)

where the potential is referenced to the SCE. The above equation shows that the aggressive effect of chloride is greater than the inhibitive effect of nitrate. According to the results, Equation (2) can be developed for 17-4PH stainless steel as:

$$E_{\text{pit}} = 259.1 + 52.1 \log \left( \frac{[\text{NO}_3^-]}{[\text{Cl}^-]^{2.83}} \right)$$ (12)

Therefore, the chloride ion concentration can deteriorate pitting behavior with the power of 2.83 in comparison to nitrate beneficial effect.

Figure 7 shows all of the results from the potentiodynamic experiments, which indicates pitting potentials in various concentrations of nitrate and chloride. The data points of pitting potentials are logarithmically plotted as a function of $[\text{NO}_3^-]/[\text{Cl}^-]^{2.83}$ in form of Equation (12). As it can be seen, the results follow a linear behavior. Furthermore, results reveal that all of the pitting
potentials are below the hump beginning potential. It means that during potentiodynamic experiments, samples that can experience a potential above 400 mV_{SCC} remain mostly passive without any pitting. This fact can be seen in Figures 4 and 5, in which linear fittings of E_{pit} versus chloride and nitrate concentrations have continued mostly until a certain potential. After this potential, pitting is rarely observed. It is in agreement with the Newman and Ajjawi’s findings which state that inhibiting effect of nitrate occurs in high anodic potential in which the pit is covered with a salt layer containing nitrate. The reduction of nitrate at the interface of salt/alloy consumes acid and thus facilitates passivation.

Equations (11) and (12) can predict the pitting potential in various concentrations of chloride and nitrate anions. When the ratio of nitrate to chloride passes a threshold value, the pitting does not occur until transition to the transpassivity happens during the potentiodynamic experiments. Figure 8 represents the concentration of nitrate

![Figure 9](image9.png)

**FIGURE 9.** The plot of the breakdown potentials versus the NO\textsubscript{3}/Cl\textsuperscript{-}\textsuperscript{1.02} ratio, which indicates the region of pitting and safe conditions. The transition threshold is about 0.35.

![Figure 10](image10.png)

**FIGURE 10.** Initial stage of pitting in 0.5 M NaCl solution (a) without nitrate and (b) with 0.005 M nitrate, which shows pits are mostly initiated from inclusions. (c) EDS analysis results of the pitted area in the 0.5 M NaCl solution, indicating Mn and S at the bottom of the pit.
versus the chloride, in which the region above the band shows the conditions that 17-4PH steel does not reveal pitting even at the elevated potentials. However, pitting occurs in the conditions with concentrations below the band. By fitting a line over the points illustrated in Figure 8, the equation of:

\[
\log \frac{[\text{NO}_3^-]}{[\text{Cl}^-]} = -0.46 + 1.02 \log \frac{[\text{Cl}^-]}{[\text{C}_138]} = 0.35
\]  

is obtained. This equation can be used as a threshold of transition from pitting conditions to the safe region. According to this equation, a critical concentration ratio of \([\text{NO}_3^-]/[\text{Cl}^-] = 0.35\) can be suggested above which pitting would not occur. Generally, for the 17-4PH stainless steel it can be said that if the ratio of \([\text{NO}_3^-]/[\text{Cl}^-] = 1.02\) is greater than 0.35, the steel remains passive until its transpassivity; however, if the ratio is lower than 0.35, pitting can occur and the pitting potential follows Equation (12).

Uhlig and Gilman have suggested the equation of \([\text{NO}_3^-]/[\text{Cl}^-] = -0.70 + 0.52 \log[\text{Cl}^-] \) for 18-8 stainless steel in chloride solution containing 1% to 15% FeCl3. In comparison with Equation (12), it is clear that in immersion pitting tests of 18-8 stainless steel in FeCl3 solution, nitrate shows greater inhibitive effect.

Figure 9 indicates the plot of breakdown potentials versus the \([\text{NO}_3^-]/[\text{Cl}^-]^{1.02}\) ratio. As illustrated, above the threshold ratio of about 0.35, transition to safe conditions occurs. In these conditions, pitting did not happen during the potentiodynamic experiments until the transpassivity potentials.

**Scanning Electron Microscope Observations**

Figures 10(a) and (b) show the SEM images of the initial stage of pit formation in chloride solution and chloride solution containing nitrate, respectively. In addition, the remnant of inclusion can be seen at the bottom of the pits. Energy

**FIGURE 11.** SEM photomicrographs of stable pits obtained from 17-4PH stainless steel polarized in (a) 0.5 M NaCl, (b) 0.5 M NaCl followed by ultrasonic preparation for 25 min in ethanol, (c) 0.5 M NaCl + 0.005 M NaNO3 without ultrasonic cleaning, and (d) 0.5 M NaCl + 0.005 M NaNO3 followed by ultrasonic preparation for 25 min in ethanol. The corrosion products can be seen in the pits before ultrasonic cleaning.
dispersive spectroscopy (EDS) of the pitted area is shown in Figure 10(c). The EDS analysis of the pit region reveals Mn- and S-rich phases, which corresponds to MnS inclusion. This observation indicates that pitting corrosion has mostly initiated from the MnS inclusions, which is in accord with the previous studies.\textsuperscript{37-39}

Figures 11(a) through (d) show the pit morphology for the chloride solution with and without nitrate ions. As depicted in this figure, in the absence of nitrate (Figures 11[a] and [b]), the pits have sharper corners in comparison with the pits formed in the solution containing nitrate (Figures 11[c] and [d]). As indicated, the corrosion products can be seen in the pit’s surface before ultrasonic cleaning (Figures 11[a] and [c]). However, no lacy cover can be observed on the pit’s mouth. After ultrasonic cleaning, the corrosion products are washed out and the pit’s surface in the solution containing nitrate is more polished and contains grain boundaries (Figure 11[d]), while the surface of stable pits in chloride solution (without nitrate) shows a rough appearance and no grain boundaries are evident (Figure 11[b]).

CONCLUSIONS

In this research, the effect of chloride and nitrate concentration on the pitting corrosion of 17-4PH stainless steel was studied. Electrochemical techniques were used to develop a relationship between ion concentrations and pitting potential. The following results were obtained:

- The results of the potentiodynamic experiments showed that the pitting potential decreases with increasing chloride and decreasing nitrate concentration. Measurements showed a linear relationship between the pitting potential and the logarithm of the aggressive and inhibitive ions concentration. According to the results, the pitting potential versus SCE follows the equation of $E_{\text{pit}} = 259.1 - 147.4 \log[\text{Cl}^{-}] + 52.1 \log[\text{NO}_3^-]$ at room temperature, when the chloride concentration ranges from 0.0025 M to 2.5 M and the nitrate concentration varies from 0.0005 M to 1 M.

- A threshold concentration ratio of $[\text{NO}_3^-]/[\text{Cl}^{-}]^{1.02} = 0.35$ is suggested; above this ratio the 17-4PH stainless steel remains passive until its transpassivity during the potentiodynamic experiments. Consequently, if the ratio is lower than 0.35, pitting occurs.

- From the potentiodynamic, it could be said that in solution containing 0.0025 M to 2.5 M chloride and 0.0005 M to 0.5 M nitrate, there is a critical potential about 400 mV\textsubscript{SCE} at room temperature, above which the 17-4PH stainless steel rarely reveals pitting in the chloride solution containing nitrate.

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