The effect of dichromate ion on the pitting corrosion of AISI 316 stainless steel Part II: Pit initiation and transition to stability

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ABSTRACT

The effect of dichromate ions on the corrosion behaviour of 316 stainless steel was investigated in 0.1 M NaCl solution by electrochemical measurements and electron microscopy. The results revealed that the addition of dichromate increases the resistance to pitting corrosion as the pitting corrosion does not occur in the presence of 0.05 M dichromate ions at room temperature. The mechanistic studies showed that the increase in pitting corrosion resistance in presence of Cr2O7^2- is due to the decrease in the metastable pit initiation, lower kinetics of metastable pit dissolution and increase in the survival probability of the pit formation.

1. Introduction

In part I of this study [1], the influence of dichromate ions on the critical pitting temperature of 316 stainless steel was assessed. Moreover, the effect of this ion on the anodic dissolution and the pit chemistry was investigated. In this part, the effect of dichromate ions on the pitting corrosion with emphasis on the pit initiation stage is investigated.

Many investigations have demonstrated that passive film breakdown and repair events may occur on stainless steels at potentials below the potential required for stable pitting [2,3]. Metastable pitting as a precursor state to stable pitting has been widely investigated [2,4,5]. Through the analysis of metastable pitting, it is possible to better understand some of the kinetic factors hindering the replacement of the passive film on stainless steels. The stability criteria for pitting may also be accurately determined [2]. The primary factor determining the stability of pitting is the local ion build up at the film breakdown sites [5]. Pistorius and Burstein [6] suggested that precipitation of a salt film on the pit bottom is necessary for pit stabilisation.

It has been long recognised that localised corrosion is a stochastic process and a statistical treatment is required to predict its initiation and growth [7]. According to the model proposed by Shibata and Takeyama [8], pits are unstable when they are first nucleated and may become stable only after they have survived past the critical age. Stochastic model of pitting introduced by Williams et al. [9] relates the probability of stable pit formation to the nucleation, death, and characteristic of metastable pits. Williams [9–11] proposed that stable pitting is the product of survival probability and metastable pitting rate. Williams et al. [9,10,12] have extended Shibata’s approaches for stable pitting to metastable pitting. Statistical approaches are easily applied since a great number of individual metastable pits can be generated. They characterised the transition from passivity to metastable pitting and then stable pitting for stainless steels.

The action of chromate ions as an effective oxidising inhibitor has been extensively studied [13–16]. Cyclic polarisation and AC impedance measurements on duplex stainless steels have shown that the addition of chromate ions shifts pitting potential toward noble values at low LiBr concentrations. It is suggested that the chromate presence favours the passive film formation by increasing the resistance of passive film at high chromate concentrations [13]. Inhibition of chloride localised corrosion of mild steel by CrO4^2- anion is reported by Refaey et al. [17]. Formation of monomeric or polyatomic oxide films on the electrode surface is generally accepted as the mechanism of chromate inhibition [15]. The effect of produced Cr2O3 has also been reported for acceleration of repassivating aluminium surface [18]. The effect of chromate ions on increasing the breakdown potential of 316 SS [16] and Aluminium AA7075-T651 [19] have been reported in NaCl solution. Burstein and Ilevbare [16] reported that chromate ions inhibit pit initiation by deactivating the possible sites and by reducing the magnitude of current transients.
Zhao and Zuo [20] reported that dichromate is effective in suppressing pit nucleation on mild steel in bicarbonate solution. Inhibition of pitting corrosion of type 904L stainless steel by dichromate ions in sodium bromide solution has been also reported [21]. Increased corrosion potential and pitting potential in the presence of \( \text{Cr}_2\text{O}_7^{\text{2-}} \) has been previously reported in the case of 2205 duplex stainless steel [22].

The mechanisms of dichromate effect on 316 SS alloy dissolution and pit chemistry were discussed in related paper [1]. In the present work, we focused on the effect of dichromate ions on the pit initiation stage of pitting corrosion and the transition from metastability to stability. The statistical evaluations were performed to investigate the effect of dichromate ions on the pitting potential, metastable pitting characterisations and the induction time of stable pitting in 0.1 M NaCl solution. In order to study the transition of metastable pitting to stability, the stability products are compared to the stability product criteria obtained from the pencil electrode results in part I [1].

2. Experimental procedure

2.1. Materials and specimens preparation

Specimens were cut from AISI 316 stainless steel bar with the following chemical composition (wt.%): 0.05 C, 0.4 Si, 1.9 Mn, 10.5 Ni, 18.1 Cr, 2.1 Mo, 0.02 P, 0.012 S, and balance with Fe. Flat samples were initially pre-passivated in 0.1 M sodium sulphate to avoid crevice corrosion at the metal/insulator interface [23], and then mounted in epoxy resin. The exposed surface area was 0.79 cm\(^2\) for potentiodynamic polarisation tests. The nucleation of individual pits and metastable pit events is not readily observable on relatively large specimens [24]. Thus, specimens with 0.2 cm\(^2\) exposed area was used for potentiostatic polarisation experiments. To study the effect of dichromate, 0.01 M, 0.03 M, and 0.05 M \( \text{K}_2\text{Cr}_2\text{O}_7 \) were added to the 0.1 M NaCl. For each test a fresh solution was utilised. All solutions were made from analytical grade regents and distilled water.

2.2. Electrochemical procedures and SEM microscopy

All electrochemical polarisation experiments were conducted at 25 °C utilising a Gill AC automated potentiostat (ACM Instruments). Electrochemical cells were composed of a platinum mesh as counter electrode and a saturated calomel electrode (SCE) as reference electrode. Electrodes were separately cold mounted in epoxy resin with a copper wire connection at the end. Prior to each test the exposed surface of specimen was ground up to 1200 grit and washed with deionised water. Prior to applying potential in each experiment, the open circuit potential (OCP) was recorded for 30 min to approach the steady-state condition potential.

Potentiodynamic polarisation measurements were conducted by sweeping the potential from 50 mV below the rest potential, at a given scan rate of 30 mV min\(^{-1}\), until the current density exceeded 300 \( \mu \text{A cm}^{-2} \) and continued to increase. The potential at which current density begins to increase, i.e. the stable pitting occurred [25], was considered as the breakdown potential [26]. Each potentiodynamic polarisation test was repeated 10 times under identical conditions. Potentiostatic polarisation method used for detection of metastable pitting current transients, which was involved polarisation of sample at 300 mV (SCE) for 1800 s and recording the current response at frequency of 40 Hz. Each potentiostatic test was repeated 5 times under identical conditions.

After checking data to be normally distributed, the pitting probability was calculated using Eq. (1) [8].

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

where \( n \) is the \( n \)th sample on which pitting occurred and \( N \) is the total number of experiments. The probability distribution function (Eq. (1)) was used for representing some other pitting characteristics as well.

A certain time period is required before the onset of the stable pitting, is known as a induction time [27]. Potentiostatic polarisation was applied to measure the survival probability of stable pit formation. To this purpose, specimens were polarised at two potentials below the breakdown potential of alloy in sodium chloride solution and in sodium chloride solution containing 0.01 M dichromate (at 350 mV (SCE) and 390 mV (SCE)) until the current density exceeded 500 \( \mu \text{A cm}^{-2} \). In these tests, the time at which the final current rise began was considered as the induction time (\(\tau_i\)) [8]. The induction time measurement was performed 30 times under identical conditions.

For scanning electron microscopy (SEM) examination, specimens were ground using silicon carbide papers from 60 to 1200 grit size and polished by 0.3 \( \mu \text{m} \) alumina paste. After potentiodynamic polarisation with the scan rate of 30 mV min\(^{-1}\) in chloride solution with and without 0.03 M dichromate addition, the samples were cleaned ultrasonically in alcohol to remove the corrosion products from pits mouths.

3. Experimental results

3.1. Electrochemical evaluation

3.1.1. Assessment of pitting corrosion probability

Typical open circuit potential–time curves obtained in chloride solution containing various dichromate concentrations are shown in Fig. 1. Examples selected are representative of the typical behaviour of alloy in various solutions. As shown, there is an increasing trend. Clearly, an increase in the concentration of dichromate shifted the OCP towards nobler values. The OCP of 316 SS after 1800 s shifted from −185.5 mV (SCE) in pure chloride solution to 167, 18.7, and 122 mV (SCE) in chloride solution with 0.01, 0.03, and 0.05 M dichromate ions, respectively. At open circuit potential, no metastable pit event was observed. Typical potentiodynamic
The cumulative probability distribution of pitting potential (\(E_{\text{pit}}\)) in 0.1 M NaCl solution with various concentrations of dichromate are shown in Fig. 3. The median value of \(E_{\text{pit}}\) (equal to \(\frac{n}{(N + 1)}\) = 0.5 [29]), as a representative of each solution condition, is 435 mV (SCE) in pure chloride solution. As observed, in the presence of 0.01 M Cr\(_2\)O\(_7\)\(^2-\), a negligible increase in the median value of \(E_{\text{pit}}\) is observed and the median value of \(E_{\text{pit}}\) is 445 mV (SCE). An improvement in pitting resistance is evident after addition of 0.03 M dichromate ions. The pitting potential increases to ca. 555 mV (SCE). It is obvious that even the maximum value of \(E_{\text{pit}}\) in plain chloride solution is less than the minimum value of \(E_{\text{pit}}\) in 0.03 M dichromate containing solution. The sufficiently high concentration of dichromate additions to chloride solution results in a great inhibiting effect against pitting corrosion occurrence in type 316 stainless steel. As it is shown in Fig. 3, no pitting was observed in the presence of 0.05 M Cr\(_2\)O\(_7\)\(^2-\) and all values of breakdown potentials for this solution exhibit transpassivity.

3.1.2. Characteristics of current transient

Metastable pits characterisations were studied to gain knowledge about the critical factors determining pitting corrosion in the presence of dichromate anion [28,29]. To study the mechanism of Cr\(_2\)O\(_7\)\(^2-\) inhibition, a series of metastable pitting experiments at constant applied anodic potential were performed. Typical current transients obtained at 300 mV (SCE) anodic potential in various solutions are shown in Fig. 4. A gradual increase of current in each event was followed by a fast drop indicating the growth and repassivation of individual unstable pits [6]. Metastable pitting was studied by observing the current transients from growth of metastable pits with peak current \(I_{\text{peak}}\) greater than 3 nA [29]. The metastable pits which were not easily distinguished from one another and the transients had overlaps, if during the repassivation of a metastable pit the corresponding current were decreased more than 50% of the peak current, it was considered as a metastable pit. Otherwise, i.e. the current decreased but less than 50% of the peak current, the overlapped events were considered as a whole metastable pit. Peak current values attributed to the metastable pits were defined by subtracting the base line current from the maximum pitting current \(I_{\text{pit}}\) [5]. Considering the background current \(I_{\text{bg}}\) in all solutions, it seems that the \(I_{\text{bg}}\) in 0.05 M dichromate is the lowest. The influence of dichromate addition on characteristics of the current transients including the frequency of metastable pit events, peak pit current and other features of current curve are discussed in detail.

3.1.2.1. Dichromate ions concentration dependence of pit initiation frequency.

Fig. 5 compares the average frequency of pit initiation as a function of time obtained from the experiments conducted in pure sodium chloride and chloride solution with various dichromate concentrations. The frequency of events was calculated by dividing the total number of current transients by electrode surface area (0.2 cm\(^2\)) and then by the time taken to record the data in each section (100 s). It is evident that the addition of dichromate leads to a decrease in metastable pit initiation frequency in a way that metastable pit frequency in the 0.05 M dichromate containing solution is lower compared to metastable frequency in other solutions. As observed, an increment in the metastable pit frequency in pure chloride solution and both 0.01 M and 0.03 M dichromate ions containing solutions, occurs after 250 s and 350 s, respectively. However, this increasing trend changes after reaching to a maximum value.

3.1.2.2. Effect of dichromate on transition from metastability to stability.

The cumulative probability distribution of peak currents determined for all metastable pits in solutions with different dichromate concentrations are plotted in Fig. 6. It is obvious that the metastable pit peak currents showed a tendency to decrease with dichromate concentration increase. The values of \(I_{\text{peak}}\), which is presented in semi-logarithmic scale, show a slight drop in solution containing 0.01 M dichromate. However, the median distribution of metastable pit peak current in the presence of 0.01 M is almost equal to the median distribution of \(I_{\text{peak}}\) obtained in pure chloride solution. Apparently, in pure chloride and in the presence of 0.01 M dichromate, there are some metastable events that their
current peaks reached to ca. 10 µA. After the addition of 0.03 M Cr₂O₇²⁻, median value of \(I_{\text{peak}}\) drops to 17 nA and the maximum amount of peak currents reaches to approximately 100 nA. In the presence of 0.05 M dichromate, the median of \(I_{\text{peak}}\) is 12 nA and no metastable pit peak current exceeds from 65 nA.

Assuming the hemispherical pits [30] and by using Faraday's second law, the metastable pit radius \(r_{\text{pit}}\) could be calculated from the charge passed during the pit growth using Eq. (2) [5].

\[
r_{\text{pit}} = \left( \frac{3M_w}{2\pi nF\rho} \right) \int_{t_i}^{t_f} \left( I_{\text{peak}} - I_{\text{bg}} \right) dt
\]  

(2)
where \( M_{\text{w}} \) is the mean atomic weight of the alloy (56.2 g mol\(^{-1}\)), \( n \) is the valence (2.16), \( F \) is the Faraday’s constant, and \( \rho \) is the mean density of the alloy (7.9 g cm\(^{-3}\)).

By comparing the probability distribution of metastable pit radii obtained in various solutions (Fig. 7), it is evident that the median value of metastable pit radius in chloride solution is almost 2 orders of magnitude higher than those obtained in solution containing dichromate. Dichromate addition remarkably reduces the median metastable pits radius from ca. 700 nm in pure chloride solution to ca. 400 nm and 350 nm in 0.01 M and 0.03 M Cr\(_2\)O\(_7\)\(^{2-}\) containing solution, respectively. It should be noted here that in the presence of 0.01 M dichromate, similar to what observed in pure chloride solution, there are lots of large pits. Metastable pits radii up to 10 \( \mu \)m are identified in solution with and without 0.01 Cr\(_2\)O\(_7\)\(^{2-}\) ion while the biggest metastable pits in the presence of 0.03 M and 0.05 M Cr\(_2\)O\(_7\)\(^{2-}\) were assessed to have ca. 1.5 \( \mu \)m radius. For a pit to maintain stable, stability product must exceed from a criteria value \([6]\). In this parameter, which is referred as \( i \cdot x \cdot \rho \) is the current density at the bottom of the growing pit and \( x \) presented the pit depth. This criterion is given by Eq. (3) \([4]\):

\[
i \cdot x = 3nFD \cdot \Delta C/2\pi
\]

where \( \Delta C \) is the difference between concentration of dissolved cations in bulk solution (i.e. pit mouth) and pit solution (\( C \)) (assuming the concentration of cations in the bulk solution to be zero, \( \Delta C \) is equal to \( C \)), \( n \) is the mean value of oxidation state of cations, \( F \) is Faraday’s constant, and \( D \) is diffusion coefficient.

The value of 3 mA cm\(^{-1}\) is determined as the criteria below which a pit can only grow as a metastable pit for 304 SS in sodium chloride solution. The \( i \cdot x \) product in a stable pit remains between 3 mA cm\(^{-1}\) and 6 mA cm\(^{-1}\) representing the concentration range of dissolved metal cations (between 75% and 150% of saturation) \([31]\).

In part I of this study \([1]\), we determined the saturation concentration of cations in the pit cavity of 316 SS in sodium chloride solution with various concentrations of dichromate. Using the values of \( D \cdot C_x \) (metal cation diffusivity times saturation concentration of metal cations essential to metal salt precipitate at the pit bottom) listed in Table 1, and by substitution of 2.16 as \( n \) (considering dissolving cations as Fe\(^{2+}\), Ni\(^{2+}\), and Cr\(^{3+}\)), the value of stability product criteria and stability product band of stable pits formed on 316 SS in various solutions can be calculated via Eq. (3).

### Table 1

<table>
<thead>
<tr>
<th>Media</th>
<th>DC(_5) (mol cm(^{-1}) s(^{-1}))</th>
<th>( i \cdot x ) value (mA cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M NaCl</td>
<td>3.28 ( \times ) 10(^{-8})</td>
<td>2.46</td>
</tr>
<tr>
<td>0.1 M NaCl + 0.01 M NaCr(_2)O(_7)</td>
<td>3.11 ( \times ) 10(^{-8})</td>
<td>2.33</td>
</tr>
<tr>
<td>0.1 M NaCl + 0.03 M NaCr(_2)O(_7)</td>
<td>2.95 ( \times ) 10(^{-8})</td>
<td>2.23</td>
</tr>
<tr>
<td>0.1 M NaCl + 0.05 M NaCr(_2)O(_7)</td>
<td>2.49 ( \times ) 10(^{-8})</td>
<td>1.89</td>
</tr>
</tbody>
</table>

**Fig. 8.** Cumulative distribution of metastable stability product in chloride solution with various concentrations of dichromate ions, obtained from potentiostatic polarisation of 316 SS in 0.1 M chloride solution with various dichromate concentrations, applied potential was 300 mV (SCE).

**Fig. 7.** Cumulative distribution of metastable pit radius in chloride solution with various concentrations of dichromate ions, obtained from potentiostatic polarisation of 316 SS in 0.1 M chloride solution with various dichromate concentrations, applied potential was 300 mV (SCE).

**3.1.3. Effect of dichromate on the survival probability of the pit formation**

Induction time for generation of stable pits was measured experimentally for 30 specimens at two distinct potentials (350 and 390 mV (SCE)) in pure sodium chloride and 0.01 M dichromate containing solution. The probability for no pit to is termed as “survival probability”. The logarithm of survival probability vs. time is plotted for chloride solution with and without dichromate at two potentials (see Fig. 9). The survival probability function, \( P(t) \), i.e. the probability of non-pitted specimen at the time \( t \), is given by Eq. (4) \([8]\).

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

where \( n \) is the number of specimens that showed pitting at any given time and applied potential and \( N \) is the total number of specimens tested. Apparently, the induction time is varied in a wide range and is not noticeably affected by potential. The induction times determined in sodium chloride solution containing 0.01 M...
Reversible equilibrium potential ($E_{eq}$) increases in the presence of Cr$_2$O$_7^{2-}$ of cathodic reaction and consequently the $E_{corr}$ is a strong oxidising agent as chromate ions [20],

$$\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} \quad (5)$$

Based on this equation, reduction of Cr(VI) to Cr(III) depends on the concentration of dichromate. The addition of dichromate ions leads to an increase in the $E_{eq}$ of cathodic reaction and consequently the value of $E_{corr}$ increases in the presence of Cr$_2$O$_7^{2-}$ [22].

It was clearly seen from potentiodynamic experiments (Fig. 2) that sufficient amount of dichromate ions significantly increases the breakdown potential ($E_b$). Furthermore, the results revealed that 0.05 M dichromate completely inhibits pitting corrosion of 316 SS at room temperature. By comparing the pitting potentials and the frequency of metastable pit events of 316 SS in various solutions, the influence of dichromate presence on pitting resistance properties can be explained. Increasing the breakdown potential can be associated with either the ability of dichromate on blocking the active sites on the surface or with the effect of dichromate on metastable pitting current transients [22]. As observed in the results of potentiostatic experiments, one of the effectiveness of dichromate as an inhibitor could lie through the enhancement of the passivity of the oxide film, making the passive film more resistant to breakdown. Comparing the current record-ings in the absence and the presence of various concentrations of dichromate ions indicates that the probability of passive film breakdown decreases with increase of dichromate concentration.

Scanning electron microscopy confirmed the electrochemical results. As shown (in Fig. 10), the number of metastable pits on 316 SS surface is significantly lower in the presence of dichromate. It has been reported that the addition of chromate decreases the average frequency of events occurred on AISI 304 and AISI 316 surface [16]. $K_{Cr_2O_7}$ is a strong oxidising agent as chromate ions [20], and the reduction of Cr(VI) to Cr(III) (Eq. (5)) as a cathodic reaction happens in the presence of dichromate ions. Thus, similar to what happens in the presence of chromate ions [16], the products of the reduction reaction in presence of dichromate ions could block the reactive sites on metal surface. The reduction reaction is likely to occur in all inhibited solution which is evident from lower passive current density in potentiodynamic polarisation curves (Fig. 2) and lower background current of potentiostatic polarisation curves (Fig. 4) particularly in the presence of 0.05 M dichromate.

Besides, based on the field assisted mechanism and by considering the competitive adsorption between chloride and dichromate ions, the inhibitor ions may make access of chloride ion to the oxide film difficult and hinder or prevent the migration of chloride ions through the passive oxide film. Consequently, the migration of Cl$^-$ toward the inclusions to active these nucleation sites will be mitigated. Furthermore, the consumption of H$^+$ by Eq. (5) can lower the localised acidity on the pit sites, as well.

Results of this study showed that dichromate ions decrease the size of the metastable pits. This is similar to the previously report-ed results on the inhibition of pitting corrosion of stainless steels AISI 304 and AISI 316 by chromate ions in acidified chloride solution [16]. Since the current density from the metastable pit transients is a measure of the rate of metal dissolution occurring...
a decrease in the peaks current indicates that dissolution within pits occurs slower in presence of dichromate ions. As discussed in previous part of paper \cite{1}, in addition to hydrogen evolution reaction, the reduction of dichromate ions to \( \text{Cr}^{3+} \) ion (Eq. (7)) may occur in the acidified pit solution \cite{33-35}:

\[
\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad E^0 = 1.33 \text{ V SHE}
\] (7)

This reaction reduces the hydrogen activity and decreases the dissolution rate within the cavities due to a decrease in acidity of pit solution.

It has been proven that measured pit solution chemistry from artificial pit electrode is a reliable step for evaluation of pit stability \cite{36}. There is a critical value, below which pit growth can only be metastable. The value of 3 mA cm\(^{-2}\) has been proposed as the critical stability product value for stable pit growth in 304 stainless steel in chloride neutral solution \cite{4}, however, as the results presented in Table 1, which are obtained from the pit growth study for the case of 316 SS in the presence of dichromate, show that the critical values of \( i \cdot x \) deviate from proposed one. The more dichromate ions are added, the less critical value for \( i \cdot x \) would be expected. Comparing the results calculated for stability product shown in Fig. 8, with the minimum values of \( i \cdot x \) (Table 1), it is clear that all metastable pits developed in dichromate containing solutions possess much lower stability products than the critical values. Therefore, in the presence of dichromate ions, the transition of metastable pits to stable pits occurs with more difficulties compared to pure chloride solution. Galvele \cite{37} suggested that pitting potential is the summation of corrosion potential in acidic pit solution, activation overpotential, extra potential required when inhibitors are presented, and the electrical potential inside the pit when ion migration is considered. According to Galvele’s model \cite{37,38}, by adding passivating inhibitor, migration of inhibitor ions into the pit cavity may cause all parameters mentioned above to be changed. The dichromate main influence was increasing the pitting potential by increasing the extra potential necessary for reaching the critical value for pit stability criterion. Since dichromate presence lowers the metal dissolution within the pit and the metastable pits radius, higher driving force is required to reach the critical stability product. In other words, in the presence of sufficient amount of dichromate ions in a constant applied potential, the potential is not adequate to cause pitting corrosion.

For the case of pure chloride solution, there are some metastable pits which hold stability product greater than the critical value. One possible explanation for such behaviour is that the assumption of hemispherical shape for metastable pits is not always true \cite{36,39}. Moreover, for these metastable pits, it is expected that the pit solution concentration has reached to a value for precipitation of a salt layer, as polished surface of such metastable pit has been shown \cite{36}.

According to the model proposed by Shibata \cite{8}, the rate of stable pit initiation (\( \chi(t) \)) is derived as Eq. (8) \cite{8}:

\[
\chi(t) = -\frac{d \ln P(t)}{dt}
\] (8)

Comparing the negative tangent of fitted curve on the \( \ln P(t) \) vs. time plot, it can be deduced that the rate of stable pit establishment is decreased in the presence of dichromate ions, which is an indication of inhibitive effect of dichromate on 316 SS. Furthermore, the slope of fitted curves in inhibited solution at both constant potentials shows that \( \chi \) varies with time which indicates that pit establishment is controlled by three or more processes \cite{8}. In these experiments, pit generation rate is not likely to be affected by applied potential. This result is inconsistent with Shibata and Takeyama \cite{8} who found that the pit initiation rate, \( \chi \), increased with the applied potential for 304 SS. Considering what reported elsewhere \cite{39}, it could be concluded that independent behaviour observed between the rate of formation of stable pits and potential may be explained by the effect of potential range which was selected for these experiments.

The dependence of pitting resistance on the rate of formation of metastable pits has been expressed by Eq. (9) \cite{40}:

\[
A = \lambda \exp(-\mu \tau_c)
\] (9)

where \( A \) is the rate of formation of stable pits, \( \lambda \) is the rate of formation of metastable pits, \( \mu \) is the repassivation probability of a metastable pits, and \( \tau_c \) is the critical time beyond which pits are considered stable if they are still active. This model is based upon the initiation and survival of the pits \cite{40}. The probability of stable pit formation is the product of the probability of metastable pit formation and the probability that the metastable pit survives to become a stable pit. The addition of dichromate ions reduces the frequency of metastable pitting. The probability of stable pit formation decreases due to the dichromate ions presence. Besides, the evaluation of kinetics data deduced from the analysis of individual current transients revealed that dichromate lowers the dissolution kinetics and consequently inhibits the transition to stability. Thus, the addition of dichromate ions to the pure chloride solution would increase the pitting corrosion resistance of 316 stainless steel. This is well consistent with the results of potentiodynamic experiments which showed that dichromate addition increases the pitting potential.

5. Conclusions

The pitting corrosion behaviour of 316 stainless steel in 0.1 M NaCl in the presence of 0.01 M, 0.03 M and 0.05 M dichromate ions as well as the correlation between pit initiation and transition of metastable pits to stable pits was studied in this paper. The results could be summarised as below:

1. Potentiodynamic tests revealed that the addition of dichromate ions to pure chloride solution, increases the breakdown potential. The addition of 0.05 M \( \text{Cr}_2\text{O}_7^{2-} \) leads to an increase in the value of \( E_b \) to transpassivity region at room temperature. It means that the pitting corrosion was inhibited in the presence of 0.05 M dichromate ions.

2. Potentiostatic tests revealed that the frequency of metastable pit formation on the surface of 316 stainless steel is decreased in the presence of dichromate ions. This result was confirmed by scanning electron microscopy. The results also revealed that the presence of dichromate ions leads to a decrease in the median values of peak pit current, pit radius, and more pronouncedly, the stability product of metastable pits formed on the 316 stainless steel surface.

3. The potentiostatic tests conducted in 0.1 M NaCl solution in the absence and the presence of 0.01 M \( \text{Cr}_2\text{O}_7^{2-} \) ion at two different potentials showed that the addition of dichromate ions leads to an increase in the survival probability of the pit. The results also indicated that the survival probability was potential independent in the applied potential range in this study.

4. The metastable pit initiation frequency and the dissolution kinetics of metastable pits were hindered by addition of dichromate ions. Both these factors decrease the likelihood of formation of stable pits in a manner that pitting corrosion was suppressed thoroughly in the presence of 0.05 M \( \text{Cr}_2\text{O}_7^{2-} \).

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