



# The effect of dichromate ion on the pitting corrosion of AISI 316 stainless steel. Part I: Critical pitting temperature



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## ABSTRACT

This article provides a better understanding of dichromate effect on the critical pitting temperature (CPT) of 316 SS in chloride solution. Potentiostatic measurements revealed that dichromate effectively improves the CPT. In the presence of dichromate ion, a remarkable decrease in the anodic dissolution in simulated pit environment and a slight decrease in the saturation concentration of cations in pit solution were defined in pencil electrode experiments. Scanning electron microscopy showed that, in compare with pure chloride solution, the pits formed on the metal surface in dichromate containing solution, have finer lacy covers.

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## 1. Introduction

To improve the pitting corrosion resistance of stainless steels in aggressive media, use of inorganic-based corrosion inhibitors has been recommended [1–7]. Inhibitors have been known to act by altering the pH or ionic content of corrosion pits, which aid in the repassivation (by oxide film formation) of a bare metal surface after the initial breakdown of the oxide film, and the blockage of the reactive sites by the formation of insoluble compounds at these sites [8–10].

The addition of chromates [11–17] and dichromate [18,19] have been reported to mitigate pitting corrosion. Illevbare and Burstein [14] investigated the effect of chromate ion on the metastable pitting occurrence in 304 SS in HCl solution. They have indicated that chromate ion prevents the adsorption of chloride ion on the passive layer by producing the bulky solid deposits above the sites of pits and/or reduce the chloride concentration within the pit sites due to the competitive adsorption between  $\text{Cl}^-$  and  $\text{CrO}_4^{2-}$  ions. The increase of corrosion potential has also been reported for the case of 25Cr duplex stainless steel in the LiBr solution containing chromate [12,13]. Chromate is a highly effective oxidising anodic inhibitor which maintains iron in the passive state, prevents breakdown and undermines the passive oxide. It is generally accepted that chromate can passivate metals by forming monatomic or polyatomic oxide films on the electrode surface [20].

It is believed that pitting corrosion occurs in three consecutive stages of passive layer breakdown, metastable pits formation,

and stable pits growth [21]. Each of these stages could be considered as the critical stage. Some researchers have suggested that using alloying elements could alter the passive layer composition and affect the pitting corrosion. Some, who believe that a pit to grow as stable pit requires passing the metastable pitting stage, have considered this stage as the most important one. Other researchers consider the pit growth as the most important stage. They believe that, pits to be able to initiate need to at least grow for a while.

It is believed that precipitation of a metal salt layer at the pit bottom is crucial for transition from metastable pit to stable pit [22]. The existence of this salt layer is confirmed thermodynamically [23]. It has been shown that the main composition of the salt precipitated within the pits formed on the Fe alloys in chloride containing solution is hydrated  $\text{FeCl}_2$  accompanied with chloride salt of other cations existed in the bulk alloy [24,25]. It has also been indicated that molybdenum has no role in the composition of salt layer precipitated in the pits formed on the surface of molybdenum containing Fe alloy [26]. In addition, it is believed that the thickness of salt layer controls its resistance [27] and decreasing the potential leads to a decrease in the salt layer thickness [28].

After Brigham and Tozer [29,30] introduced a particular temperature as the criterion of resistance to pitting corrosion below which no stable pit could be formed (i.e. critical pitting temperature), researchers have investigated the effect of different variations on the critical pitting temperature of stainless steels [31–35]. The effect of dichromate ion on the corrosion behaviour of 2205 duplex stainless steel in 0.1 M NaCl solution was investigated by Ebrahimi et al. [18]. It was shown that the presence of

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dichromate ion increases the critical pitting temperature of 2205 duplex stainless steel. Researchers have tried to suggest a definition of CPT [15,36]. Considering the variation of diffusion limiting current density ( $i_{lim}$ ) in the presence of salt film at the pit bottom and the maximum current density essential for passivity in the pit solution ( $i_{max}$ ) with temperature, Salinas-Bravo and Newman [36] have considered the CPT as the temperature at which these two variations are equal (i.e.  $i_{lim} = i_{max}$ ).

Limited researches were performed to investigate the effect of maximum current density on the CPT. For instead, the decrease in the  $i_{max}$  has been reported as the reason of the observed increase in the value of CPT of 2205 duplex stainless steel in the presence of nitrate ion [7].

The influence of different ions on the diffusion limiting current density and pit chemistry has been more interested [37–39]. Using pencil electrode, researchers assessed the value of limiting current density. They have investigated the effect of pit chemistry on the CPT [37–40] using Eq. (1) proposed based on Fick's First law [23].

$$i_{lim} = \frac{nFD C_s}{\delta} \quad (1)$$

where  $i_{lim}$  represents the diffusion limiting current density,  $F$  is the Faraday's constant,  $D$  is the cations diffusion coefficient,  $C_s$  is the saturation concentration of metal cations necessary for metal salt to precipitate and  $\delta$  is the pit depth. Investigation on the effect of sulphate ion on the CPT of different types of stainless steels has revealed that addition of this ion decreases the CPT, though increases the pitting potential at the temperatures above CPT [37,39]. The decrease in the value of CPT was suggested to be related to the decrease in the value of saturation concentration crucial for metal salt precipitation and its consequent decrease in the value of limiting current density. Recently, we studied the effect of thiosulphate using pencil electrode method, and showed that this ion has the same effect as sulphate in deterioration of the CPT of 316 SS [41].

It has been proposed that the increase in pitting potential at temperature above CPT, was related to the increase in the proportion of  $C^*/C_s$  where  $C^*$  is the critical concentration of metal cations within the pit essential for a pit to be remained. Since an increase in the value of this proportion (toward 1) leads to facilitate passivation near the pit mouth, the lacy cover formed on the pit surface would have finer holes [37–39].

In the present study, the effect of dichromate ion on the corrosion behaviour of AISI 316 stainless steel was investigated. In this part, we first studied the effect of dichromate ion ( $Cr_2O_7^{2-}$ ) on the critical pitting temperature of 316 stainless steel in 0.1 M NaCl solution in the presence of 0.01 M, 0.03 M and 0.05 M dichromate ion by employing potentiostatic polarisation experiments. Next, a mechanistic approach was arranged based on the model of CPT proposed by Salinas-Bravo and Newman. For this purpose, the effect of dichromate ion on the limiting current density in 0.1 M NaCl solution and on the maximum current density necessary for passivity in a simulated pit solution (5 M HCl solution) were investigated using pencil electrode. SEM analysis was utilised to study the effect of dichromate ion on the structure of the lacy cover formed on the pit mouth. The effect of dichromate ion on the pitting potential and the initiation of metastable pitting are presented in part II of this study.

## 2. Experimental procedure

### 2.1. Materials and preparations

CPT experiments were performed on type AISI 316 stainless steel. Rod-shaped samples with 4 cm<sup>2</sup> surface area were wet ground to 1200-grit finish. To confirm that only definite pitting was occurring, precise inspections were performed using a stereo microscope after each test. For pencil electrode studies to measure the pit propagation rate and to estimate the pit chemistry in chloride/dichromate solutions, 50 μm diameter 316 stainless steel wire was used. Pencil electrodes were prepared by mounting the wire in epoxy resin with one cross-sectional surface exposed to test solution. Exposed surface of pencil electrodes were ground to 60 grit. Alloy compositions of materials used in this study are listed in Table 1.

The base solution was 0.1 M NaCl. To study the effect of dichromate ion, dichromate in the form of  $K_2Cr_2O_7$  was added to 0.1 M NaCl solution. A saturated calomel electrode (SCE) as a reference electrode and a platinum mesh as a counter electrode were used for all electrochemical experiments.

### 2.2. Electrochemical procedure

To employ potentiostatic polarisation in CPT determination, the specimens were polarised at 750 mV (SCE) and the solution temperature was increased at the rate of 0.6 °C min<sup>-1</sup> until the current density reached to 300 μA cm<sup>-2</sup>. The CPT value was considered as the temperature at which current density began to increase gradually [33].

Anodic dissolution was assessed by potentiodynamic polarisation tests in 5 M HCl at various temperatures using pencil electrodes [42]. The specimens were placed in an electrochemical cell facing upwards. After obtaining stable condition, polarisation curves were recorded at a sweep rate of 300 mV min<sup>-1</sup>. The aim of selecting electrodes with very small diameter was simulating the single corrosion pit.

For measuring the chemistry of pit, pencil electrodes were exposed to the 0.1 M NaCl solution facing upward to avoid venting of precipitated salt and preventing the convection within the pit [24]. The electrodes were potentiostatically polarised for 600 s at 700 mV (SCE) to create a single corrosion pit at temperature of 25 °C. Subsequently, the potential was ramped to the passive region at a sweep rate of 60 mV min<sup>-1</sup>. At initial time period of applying potential in artificial pit experiments, small pits are formed on the surface, then coalesce and make a single corrosion pit. Since it was impossible to create a single corrosion pit in the presence of dichromate ion, a single pit was generated in pure chloride solution and 50 s after commencing the test, dichromate was added to the solution. Once the dichromate was added, applying the potential was stopped and started instantly to insure that the previously formed salt, which is formed in the absence of dichromate, is completely dissolved and new salt is produced at the pit bottom. This procedure was identical in all experiments. The pit depth was calculated by applying Faraday's second law (Eq. (2)) [43]:

$$\delta = \frac{M_w}{nF\rho} \int idt \quad (2)$$

**Table 1**

Chemical composition of alloy 316 SS (wt.%). (a) Bulk material used for CPT measurements and (b) 50 μm dia. wire used for pencil electrode studies.

Metal	C	S	P	Si	Mn	Ni	Cr	Mo	Fe
Bulk alloy	0.05	0.012	0.02	0.4	1.9	10.5	18.1	2.1	Bal.
50 μm dia. wire	0.045	0.015	0.019	0.5	2.1	10.8	18.7	2.05	Bal.

where  $M_w$  is the mean atomic weight,  $n$  is the average valency of cations (assuming stoichiometric dissolution of Fe, Cr and Ni,  $n$  is considered to be 2.16), and  $\rho$  is the average alloy density.

Decreasing the potential causes the salt layer to be vanished at a specific current density at which the concentration of cations becomes less than the cation saturation concentration essential for salt precipitation. The current density attributed to the potential at which the salt layer is dissolved is considered as the limiting current density ( $i_{lim}$ ). Considering the value of diffusion controlled limiting current density obtained from  $i-t$  curve in each solution, the values of  $DC_s$  was calculated using the formula proposed based on Fick's First law (Eq. (1)) [23]. The artificial pit tests were carried out at ambient temperature.

To study the effect of dichromate ion on the morphology of lacy metal cover over the stable pits, grinding to 1200-grit was performed on flat samples. Then, potentiostatic polarisation (at the 700 mV (SCE)) was performed. Sample surfaces were washed with alcohol and dried. Some samples were subjected to an ultrasonic bath to remove the metal cover. The formed pits were examined by scanning electron microscopy.

### 3. Experimental results

#### 3.1. Electrochemical evaluations

##### 3.1.1. Critical pitting temperature

Fig. 1a illustrates the typical current density vs. time curves obtained from potentiostatic polarisation at 750 mV (SCE) at various concentrations of dichromate ion. The CPT was defined as the temperature at which the final current rise began, indicating the onset of stable pitting [33]. The critical pitting temperature of 316 SS in various test solutions is presented in Fig. 1b. Error bars represent 95% confidence limits measured from at least five experimental tests under the identical condition. As observed, the higher the concentration of dichromate, the higher the CPT of 316 SS. As can be seen, the CPT of 316 SS is 6 °C in pure chloride solution. The addition of 0.01 M and 0.3 M dichromate leads to an increase in the CPT value to 9 °C and 19 °C, respectively. A great inhibition was found in the presence of 0.05 M  $Cr_2O_7^{2-}$  such that the critical pitting temperature of alloy increases up to 38 °C.

##### 3.1.2. Measurement of dissolution kinetic in simulated pit solution

Fig. 2 shows the polarisation behaviour of 316 SS obtained in 5 M HCl in the absence and the presence of 0.05 M  $Cr_2O_7^{2-}$  ion at  $-5$  °C (for instance). In the presence of dichromate ion, the corrosion rate ( $i_{corr}$ ) is significantly higher. The mean value of  $i_{corr}$  obtained in pure HCl solution is ca.  $0.03 \text{ mA cm}^{-2}$  which increased to ca.  $70 \text{ mA cm}^{-2}$  in the presence of 0.05 M dichromate. The corrosion potential is also increased by dichromate addition (from approximately  $-315 \text{ mV (SCE)}$  to approximately  $-220 \text{ mV (SCE)}$ ).

Anodic polarisation curves obtained from potentiodynamic polarisation in 5 M HCl and 5 M HCl + 0.05 M  $Cr_2O_7^{2-}$  solution at various temperatures are shown in Fig. 3. In both solutions, the anodic polarisation curves at temperatures of  $-5$  °C and 0 °C, show the same active regions followed by active-passive transition occurring at comparable potentials near 400 mV (SCE). At higher temperatures, the effect of this ion on current response was somehow different. After the maximum current was reached, a noisy plateau region was observed. At higher potentials, the current density returned to the current density corresponding to passivity. At temperatures of  $-5$  °C and 0 °C, in dichromate containing solution, a very small noisy plateau region is observable before passive state.

Comparing the curves, it can be observed that, the potential at which passivity occurs is generally increased by dichromate addition. Furthermore, by comparing the results presented in Fig. 3a

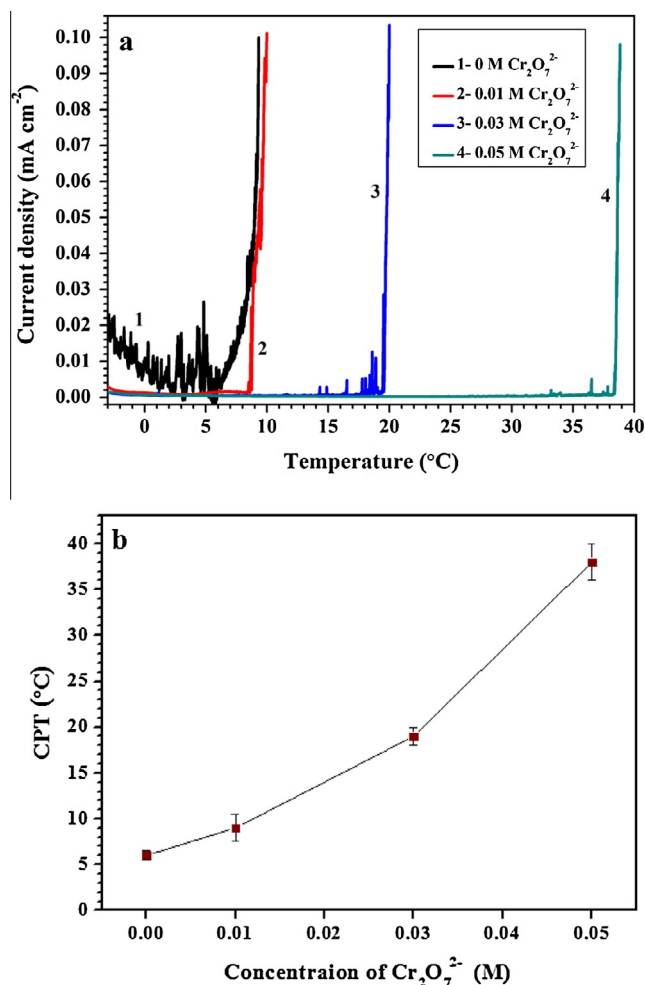


Fig. 1. The results of potentiostatic polarisation of 316 SS at 750 mV (SCE) in 0.1 M NaCl solution with different concentrations of dichromate ion and temperature increasing rate of  $0.6 \text{ °C min}^{-1}$  (a) Current density-time responses, (b) CPT values, Error bars represent 95% confidence limits measured from at least five runs under identical conditions.

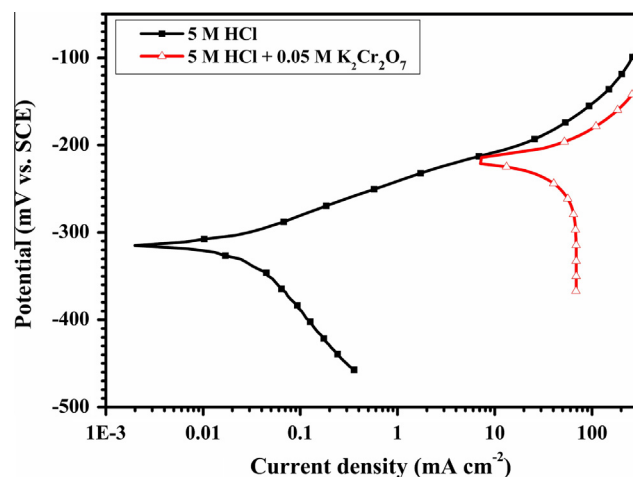


Fig. 2. Potentiodynamic polarisation curves for 316 SS pencil electrode, obtained from potentiodynamic polarisation in 5 M HCl, and 5 M HCl + 0.05 M  $K_2Cr_2O_7$  solutions at 25 °C. The sweep rate was  $300 \text{ mV min}^{-1}$ .

and b, the effect of dichromate ion on lowering the dissolution rate in the active region at all temperatures is evident. These results are used for investigating the effect of dichromate ion on the maximum

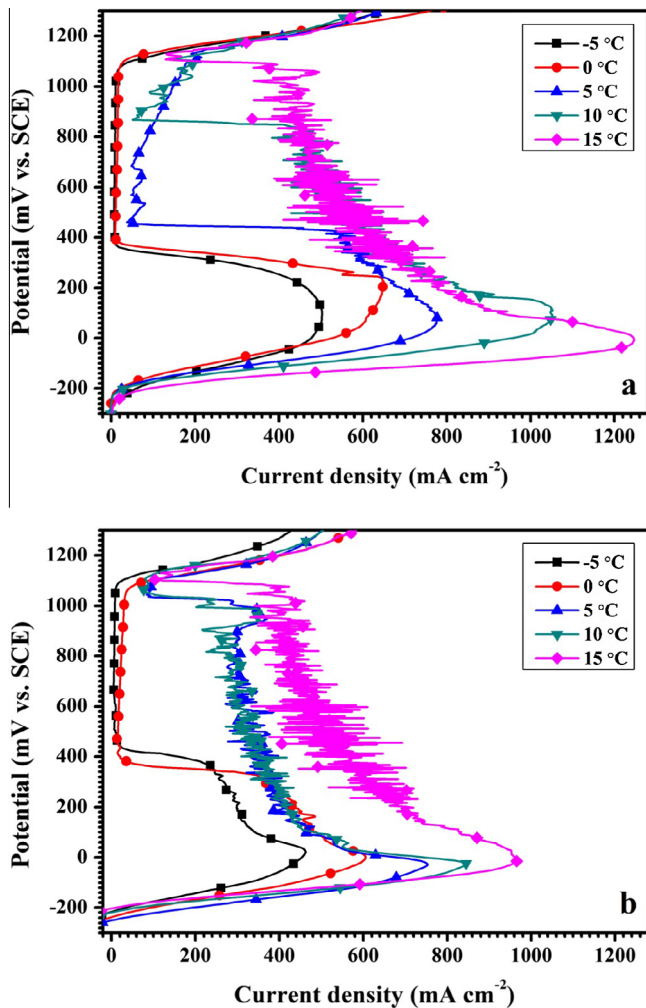


Fig. 3. Current density–potential curves for 316 SS pencil electrode, obtained from potentiodynamic polarisation in (a) 5 M HCl, and (b) 5 M HCl + 0.05 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions at different temperatures. The sweep rate was  $30 \text{ mV min}^{-1}$ .

current density of 316 SS. The values of maximum current densities ( $i_{\text{max}}$ ) in the absence and the presence of dichromate ion are shown in Fig. 4. The best lines were fitted to the mean values of  $i_{\text{max}}$  in each medium. Curves of  $i_{\text{max}}$  vs. temperature have increasing trend in both solutions. The most important result of this experiment was that both the values of maximum current densities and the slopes of linear fit decrease by dichromate addition.

### 3.1.3. Saturated concentration of metal cations within pit

The effect of various concentrations of dichromate ion on the pit chemistry was investigated to get further understanding of the role of this anion on the propagation stage of pitting of 316 SS.

Typical current vs. time curve obtained in pure chloride solution is shown in Fig. 5. The overall shapes of current density–potential in solutions containing various concentrations of  $\text{Cr}_2\text{O}_7^{2-}$  are the same. At the initial time periods, small pits are formed on the surface, and then coalesce with each other making a single corrosion pit. When the current flow is interrupted, the concentration of metal chloride at the interface falls and the salt layer dissolves immediately [44] which leads to a sharp drop in current density. On reapplying the potential, a high current flows as there is no longer an impeding salt layer, and the process of supersaturation and precipitation of the salt layer is repeated [24]. The peak observed in the  $i-t$  curve just after the current density drop could be related to the cations supersaturation happened within the pit solution [39].

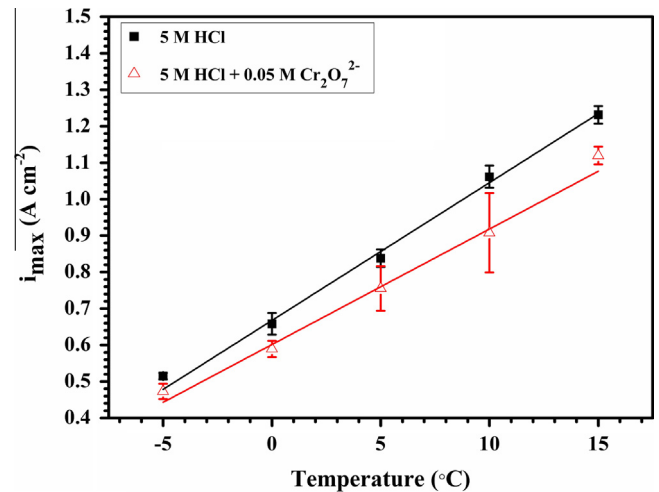


Fig. 4. The values of maximum current density for  $50 \mu\text{m}$  dia. 316 SS pencil electrode, obtained from potentiodynamic polarisation in simulated pit solution in the absence and the presence of  $0.05 \text{ M K}_2\text{Cr}_2\text{O}_7$  at different temperatures alongside of best fitted lines to the mean values of maximum current density. Error bars represent 95% confidence limits measured from at least five experiments under identical conditions.

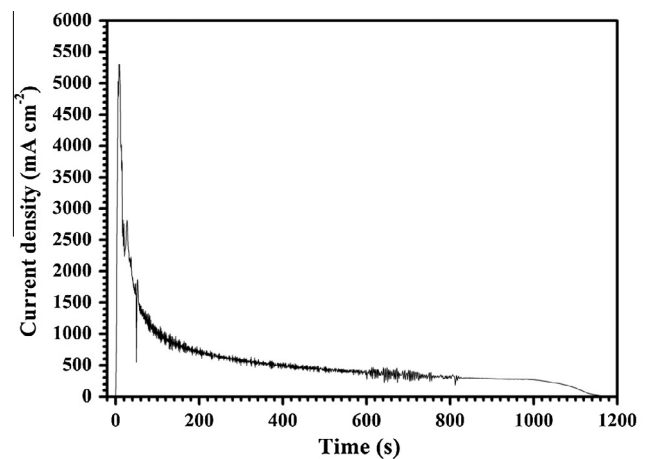


Fig. 5. Current density vs. time curves for  $50 \mu\text{m}$  dia. 316 SS pencil electrode obtained from potentiodynamic polarisation conducted after potentiostatic test from anodic potential of  $700 \text{ mV (SCE)}$  to corrosion potential with the scan rate of  $-60 \text{ mV min}^{-1}$  in  $0.1 \text{ M NaCl}$  solution at  $25 \text{ }^\circ\text{C}$ .

Fig. 6 represents a current density vs. pit depth curve obtained from potentiostatic step of the pencil electrode experiments conducted in  $0.1 \text{ M NaCl}$  and  $0.1 \text{ M NaCl} + 0.05 \text{ M Cr}_2\text{O}_7^{2-}$  solutions. The linear relationship between the second power of current density and the reciprocal of time confirmed the diffusion control regime in this region. As observed, the current density drops slowly with pit depth in both solutions. A possible reason suggested for this observation is that the thickness of salt film increases as the pit deepens and the diffusion path increases with time [24]. Furthermore, it is apparent that the current density in dichromate containing solution is less than the current density of  $0.1 \text{ M NaCl}$  solution. Note too, that the fluctuations, observed in both  $i-t$  curves depicted in Fig. 6 for  $0.1 \text{ M NaCl}$  in the absence and the presence of dichromate ion, are reproducible. Fluctuations observed in dichromate containing solution have higher amplitude. These fluctuations could be related to the passivation and reactivation of active sites under the salt layer [7,45].

As the salt film is present, the steady current density is controlled by diffusion and consequently is potential independent

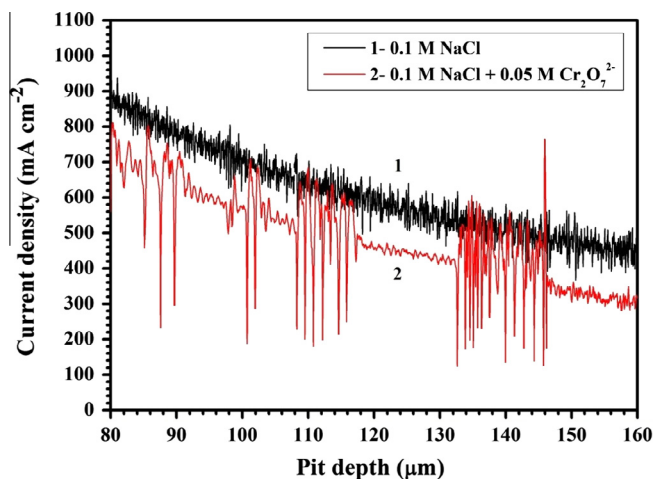


Fig. 6. Current density vs. pit depth curves for 50  $\mu\text{m}$  dia. 316 SS pencil electrode, obtained from potentiostatic polarisation conducted at applied anodic potential of 700 mV (SCE) in 0.1 M NaCl, and 0.1 M NaCl + 0.05 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions at 25  $^\circ\text{C}$ .

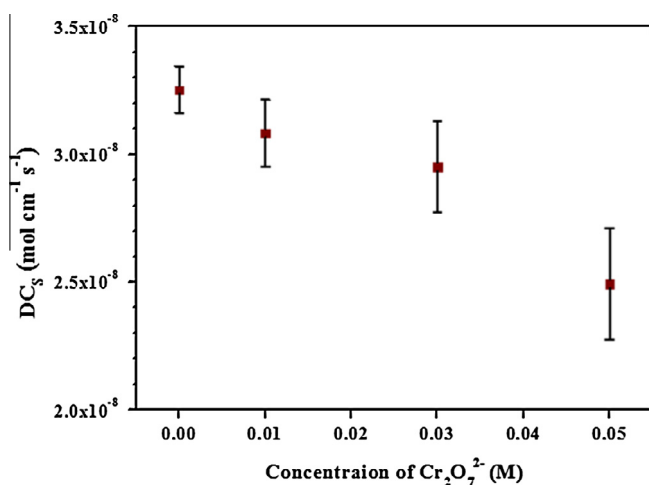


Fig. 7. The values of  $D \cdot C_s$  vs. dichromate concentration for 50  $\mu\text{m}$  dia. 316 SS pencil electrode, obtained from current–time curves at 25  $^\circ\text{C}$ . Error bars represent 95% confidence limits measured from at least five experiments under identical conditions.

[24]. Thus, in the absence of salt layer, the dissolution regime changes from diffusion controlled to the activation controlled [46–48]. The values of  $D \cdot C_s$  were calculated by considering the limiting current density (i.e. the current density attributed to the

potential at which the salt layer is entirely dissolved) and using Eq. (1). The values of  $DC_s$  in various concentrations of dichromate ion in the bulk solution are shown in Fig. 7. Apparently, the saturation concentration of metal salts decreases with the dichromate concentration increase. The average of  $DC_s$  value of dichromate free solution is  $3.25 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$ . In the presence of 0.01 M and 0.03 M  $\text{Cr}_2\text{O}_7^{2-}$ , a slight decrease in the saturation concentration of metal cations is observed and  $DC_s$  is defined as  $3.08 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$  and  $2.95 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$ , respectively. Addition of 0.05 M dichromate causes the  $DC_s$  value to decrease to  $2.49 \times 10^{-8} \text{ mol cm}^{-1} \text{ s}^{-1}$ . Thus, the effect of dichromate on concentration of metal salts is more pronounced at the presence of sufficient concentration of this anion.

### 3.1.4. SEM observation of morphology of stable pits

Fig. 8 shows the typical morphology of a stable pit formed in pure chloride solution. A layer covering the pit with a number of holes distributed around the pit mouth (shown in Fig. 8a) is a remnant of the passive film [22] referred to as the pit cover and has been shown to play a crucial role in pit stability [49]. Fig. 8b represents the morphology of this pit after the cover removal. To investigate the effect of dichromate ion, the lacy metal cover over the pit formed in solution containing dichromate was also investigated (Fig. 9a). By comparison, it is obvious that the lacy cover of pits mouths formed in dichromate containing solution has finer perforation compared to lacy cover of the pits formed in dichromate free solution. The morphology of these pits after the cover removal is depicted in Fig. 9b.

## 4. Discussion

### 4.1. The possible mechanisms for the effect of dichromate on the CPT

Our observations suggest that addition of dichromate ion to chloride solution increases the CPT of 316 SS. According to the definition proposed by Salinas–Bravo and Newman [36], the diffusion controlled current density and the maximum current density essential for passivity are two factors which affect the critical pitting temperature.

The results of the experiments performed in simulated pit solution demonstrate that the presence of dichromate leads to an increase in the pitting corrosion and a decrease in the maximum current density of alloy. Lower maximum current density is consistent with the observations of Ebrahimi et al. [18] who showed that the maximum current density of 2205 duplex stainless steel in 5 M HCl decreases in the presence of  $\text{Cr}_2\text{O}_7^{2-}$  ion at 25  $^\circ\text{C}$ .

According to the literature, the pH of solution within the pit is totally different from the bulk solution and has a range between

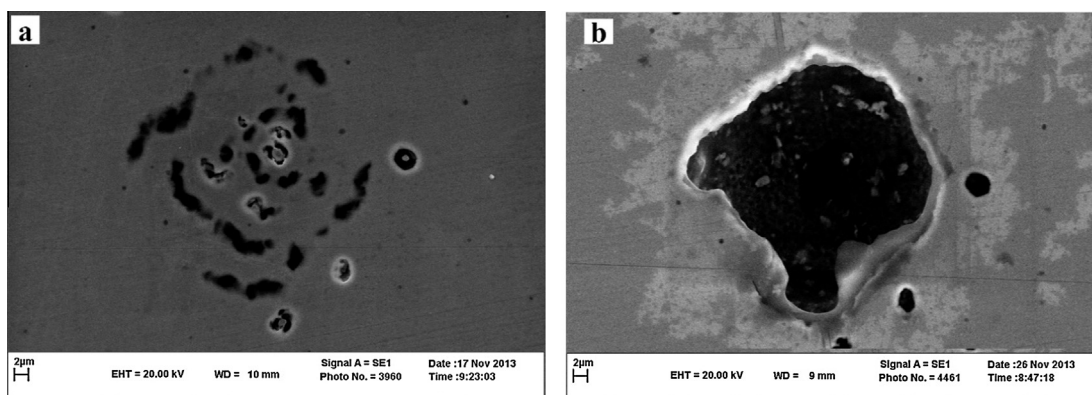
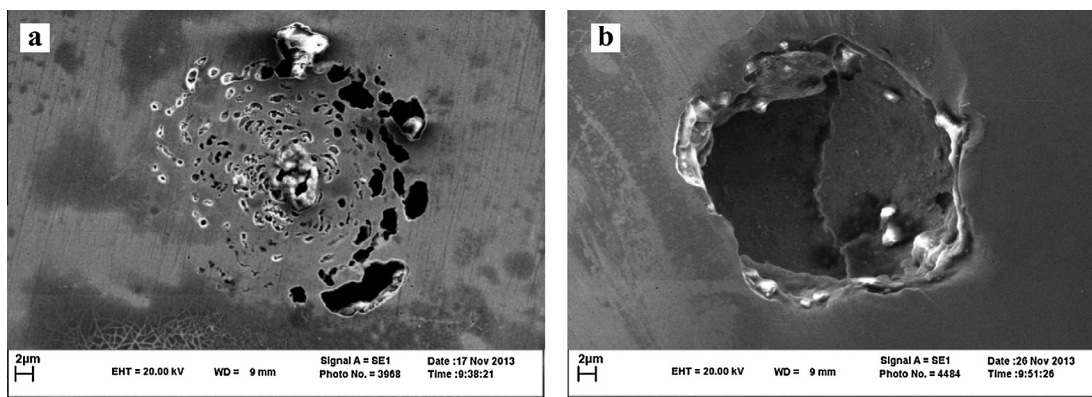


Fig. 8. SEM micrographs of a stable pit after potentiostatic polarisation at 700 mV (SCE) in 0.1 M NaCl solution at 25  $^\circ\text{C}$ . (a) Morphology of lacy cover and (b) morphology of pit after removal of lacy cover (after ultrasonic cleaning).

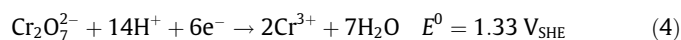


**Fig. 9.** SEM micrographs of a stable pit after potentiostatic polarisation at 700 mV (SCE) in 0.1 M NaCl + 0.1 M dichromate solution at 25 °C. (a) Morphology of lacy cover and (b) morphology of pit after removal of lacy cover (after ultrasonic cleaning).

3 and negative values due to hydrolysis of the metal ions [50–52]. The main explanation for decreased acidity within a natural and artificial pits is the increase of  $H^+$  ion activity [51]. In 5 M HCl solution, which is considered as the pit solution [7,42], the cathodic reaction assumes as below:



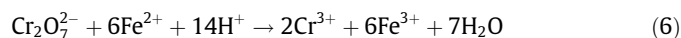
In addition to Eq. (3), The reduction of dichromate (VI) ion is suggested for cathodic reaction as follows [53,54]:



The relevant anodic half reaction for dichromate reduction is:



and the total reaction is:



Because of higher value of reversible equilibrium potential of dichromate reduction reaction, the observed increase in the corrosion potential ( $E_{corr}$ ) (Fig. 3) seems reasonable.

We suggest that the mitigated active dissolution is attributed to the reduced acidity in the presence of dichromate ion. Based on Eq. (6), the reduction of dichromate ions consumes hydrogen ions and consequently increases the solution pH. Considering the overall reaction (Eq. (6)), it is obvious that 1 mol dichromate consume ca. 14 mol  $H^+$  which leads to an increase in solution pH.

It should be noted that the hydrolysis of metal cations are pH dependent. It is well known that  $Cr^{3+}$  (formed in Eq. (4)) is generally found at low pH and only at extremely high pH is  $Cr(OH)_4^-$  formed [55]. In the simulated pit solution, which the pH is near zero, Cr (III) would mainly present in the form of  $(Cr^{3+})_{aq}$  and only partial hydrolysis occurs. Likewise, in this low pH condition, only a portion of Fe (III) participates in hydrolysis reaction and the main product of oxidation of  $Fe^{2+}$  is considered to be  $Fe^{3+}$  (aq) [55]. Therefore, in comparison to the pH increase, which occurs via Eq. (6), the decrease in pH, which occurs as a consequence of hydrolysis of these produced ions, would be small. We can therefore conclude that higher pH in the presence of dichromate may be the probable reason for decreased active dissolution in an incipient pit.

The plateau region observed in the polarisation curves could be an indicative of the diffusion controlled current density and is consistent with the results for the nitrate ion effect in the HCl media reported by Newman and Shahrabi [42] and by Zakeri and Moayed [7]. The fluctuations existed in the plateau region, is in agreement with the literature [7,45] and can be attributed to the localised activation and repassivation occurred under the salt film.

At temperatures above 0 °C, we observed that the passivity occurs despite the presence of salt film at the surface which is due to the passivation under the salt film [45]. The increase in the temperature leads to an increase in the potential at which the current density returns to the passivity region. Higher passivity potential under the salt film can be attributed to an increase in the thickness of the salt layer at higher temperature which leads to higher potential drop across the salt film.

Considering the results of potentiodynamic polarisation in 5 M HCl in the absence and the presence of dichromate ion, the value of  $i_{max}$  decreased in the presence of this ion. Based on the CPT definition proposed by Salinas-Bravo and Newman (i.e. the temperature at which  $i_{lim} = i_{max}$ ) and ignoring the effect of this ion on limiting current density, addition of dichromate ion would lead to an increase in the value of CPT of 316 SS. In other words, since the presence of dichromate ion leads to a decrease in the dissolution kinetics of 316 SS, therefore the temperature should be increased to compensate this decrement to a pit becomes stable.

In the remainder of this section, the effect of dichromate on the pit chemistry is discussed. The results of pencil electrode experiments demonstrated that the addition of dichromate ion decreases the saturation concentration of the cations essential for metal salt precipitation within the pit. Decline in the value of  $DC_S$  which happens in the presence of dichromate (maximum concentration of dichromate ion added), affects the salt precipitation. The lower value of  $DC_S$  in the presence of dichromate ion could be explained based on the reactions occur in the presence of dichromate ion (Eq. (6)). According to this equation, in highly acidic pit solution, dichromate ion is reduced to  $Cr^{3+}$ . It is believed that the salt precipitated at the bottom of pit formed on the 316 SS surface, is enriched from  $Fe^{2+}$  alongside of  $Cr^{3+}$  and  $Ni^{2+}$  in their stoichiometric proportion in the bulk alloy [24]. The partial hydrolysis of  $Cr^{3+}$  occurs in the presence of dichromate ion may lead to an increase in the proportion of  $CrCl_3$  salt.

The other cation, which may contribute in salt precipitation in dichromate containing solution, is  $Fe^{3+}$ . Therefore, it is predicted that in the presence of dichromate ion, in addition to metal salts precipitated at the bottom of pit in pure NaCl solution, further amounts of  $CrCl_3$  would precipitate. The other probable reason for lower solubility of salt in solution containing dichromate may be attributed to the contribution of ferric ion in salt precipitation. As mentioned above, ferric ion is the product of oxidation of  $Fe^{2+}$  in the presence of dichromate. Due to the changes in the salt composition, it seems that the precipitation of salts is facilitated and subsequently the reduction in the saturation concentration of cations seems reasonable. It is believed that the presence of metal salt is necessary for a metastable pit to transform to stable pit [22]. It can be concluded that dichromate addition provides the proper

condition for salt precipitation at lower temperatures. Thus, the temperature at which stable pitting occurs (CPT) is likely to decrease in the presence of dichromate ion. Based on Eq. (2), a decrease in  $DC_S$  value in the presence of dichromate ion leads to a decrease in the value of diffusion controlled limiting current density. Based on the CPT theory, which introduces the critical pitting temperature as the temperature at which the limiting current density is equal to the maximum current density, and by considering the effect of dichromate addition in decreasing both  $i_{\max}$  and  $i_{\lim}$ , a change in each parameter would lead to a change in the CPT. In the presence of dichromate, the decreased limiting current density is predicted to deteriorate the CPT. On the other hand, a decrease in  $i_{\max}$  would lead to an increase in the critical pitting temperature of 316 SS. Considering the increase in the value of CPT of 316 SS in the presence of dichromate ion, it could be concluded that the decrease in  $i_{\max}$ , compensates the effect of  $i_{\lim}$  on the CPT of 316 SS. Therefore, in the presence of dichromate ion, the temperature at which  $i_{\lim}$  and  $i_{\max}$  are equal (i.e. CPT), is shifted to higher values. In other words, this is the lower maximum current density which leads to increase observed in the critical pitting temperature in the presence of dichromate ion.

However, based on the decreased maximum current density in the presence of dichromate, the higher CPT value of alloy in dichromate containing solution is reasonable, but the increase in the alloy CPT in the presence of dichromate (32 °C increase in presence of 0.05 M dichromate, for instance) is truly considerable, which could not be fully explained based on the presented results (because of the deleterious effect of dichromate ion on the diffusion controlled limiting current density). From the point of view of the necessity of pitting initiation as the first stage of pitting, the ability of dichromate to blockage of the active sites at higher temperatures and also the retardation in the establishment of stability criterion into higher temperatures may be the probable reasons for higher CPT in the presence of dichromate. The effect of dichromate ion on the pit initiation on the 316 SS was studied in part II of this study. However, a comprehensive research is required to prove any other mechanism involved.

#### 4.2. SEM observation of morphology of stable pits

Scanning electron microscopy showed that the lacy cover formed over the pits in dichromate containing solution have constricted openings in when compared to the lacy cover of pits in pure NaCl solution. Changes in lacy cover pore size may be due to the change in the critical concentration of metal cations necessary for the pit to remain stable ( $C^*$ ) within the pits formed in dichromate containing solution. In the undercutting process, metal in the pit bottom continually dissolves while the pit solution near the pit mouth may become too dilute and metal in this area re-passivates [37]. When the value of  $C^*$  is high, but not exactly equal to the saturation value, passivation near the pit mouth will be easier. As a result, the size of the holes in the cover will be decreased. The higher  $C^*/C_S$  in the presence of dichromate is a probable reason for decreased size of holes in the lacy cover over the pits. However, the evaluation of the effect of dichromate ion on the value of  $C^*/C_S$  was not interested in this study.

## 5. Conclusions

In this research, the effect of dichromate ion on the critical pitting temperature of 316 stainless steel was investigated and the mechanism of dichromate effect on the CPT was explored. The results could be summarised as below:

1. Results obtained from potentiostatic polarisation tests revealed that addition of dichromate ion to 0.1 M NaCl solution leads to an increase in the critical pitting temperature of 316 stainless steel. By addition of dichromate ion, the mean value of 316 SS CPT changes from 6 °C in 0.1 M NaCl solution to 38 °C in 0.1 M NaCl + 0.05 M dichromate solution.
2. Experiments conducted in simulated pit solution showed that the addition of  $Cr_2O_7^{2-}$  decreases the anodic dissolution of alloy and accordingly decreases the maximum current density which may be due to the influence of dichromate on lowering the pH of pit solution. It was also revealed that dichromate ion has no inhibiting effect on the salt covered surface.
3. Pencil electrode results obtained from chloride solution with and without dichromate addition revealed that the saturation concentration of metal salts and the diffusion controlled limiting current density decreases by dichromate addition. In other words, dichromate ion facilitates the precipitation of metal salts due to lowering the saturation concentration of cations essential for salt precipitation
4. The results of these experiments lead to the conclusion that the decrease in anodic dissolution in the presence of dichromate is the dominant factor causing higher CPT.
5. SEM observation revealed that the pores in lacy cover over the pits formed in the presence of dichromate are in smaller size compared to the pores formed in pure chloride system.

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