



## Critical pitting temperature dependence of 2205 duplex stainless steel on dichromate ion concentration in chloride medium

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### ABSTRACT

In this study, influence of various concentrations of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) and chloride ions on critical pitting temperature (CPT) of duplex stainless steel 2205 (DSS 2205) is investigated by employing potentiodynamic and potentiostatic CPT measurement methods. Potentiostatic results indicate that by adding 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  to 0.1 M NaCl solution the CPT raised by 12 °C. Based on potentiodynamic CPT measurements in the solution of  $(\text{Cr}_2\text{O}_7^{2-})/(\text{Cl}^-)$  ratio equal to one for solutions containing 0.1 M NaCl + 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  and 0.01 M NaCl + 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$ , no CPT was detected up to 75 °C.

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### 1. Introduction

Duplex stainless steels (DSS) are iron-based alloys that possess a two phase microstructure: austenite and delta ferrite in approximately similar percentages; hence they combine attractive properties of austenitic and ferritic stainless steels [1–4]. Owing to these great properties, DSS are of interest for various applications, such as petroleum, gas refineries and marine environments particularly due to their combination of corrosion and mechanical properties [1–8]. The corrosion resistance of a passivated metal is often determined by its susceptibility to local breakdown and to initiation of pits. It has been demonstrated [9] that the growth of corrosion pits occurs in two consecutive stages characterized by a metastable growth in the early period, followed by a stable growth. Pitting corrosion is a deleterious corrosion type which may cause a major failure in industrial applications. Critical pitting temperature (CPT) was first introduced by Brigham and Tozer [10–12] and it is defined as the lowest temperature at which stable propagating pitting occurs under specified test condition on the test surface [13]. Pitting corrosion is recognized as an insidious type of attack that results in many unexpected failures of metallic structures. The pitting corrosion of metals and alloys occurs when passivity breaks down at local points on the surfaces exposed to corrosive environments containing aggressive anions [14,15]. At these points, anodic dissolution proceeds while most of the surface remains passive.

To encompass a higher temperature application and to improve the pitting resistance of stainless steels in halide media, use of

inorganic-based corrosion inhibitors have been recommended [2,3,14,16]. 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 reactive sites by the formation of insoluble compounds at these sites [17–19]. Addition of  $\text{MoO}_4^{2-}$  oxy-anions inhibits the pitting corrosion and causes the CPT to increase [20]. Sulphate is a conventional inhibitor of chloride-induced pitting of stainless steel and increases pitting potential towards noble values [21]. Based on investigations on the effect of  $\text{SO}_4^{2-}$  on the CPT, a detrimental effect was reported by Moayed [22], while a contradictory behaviour was demonstrated by Deng [23]. It has been known for some time that chromate is a very efficient inhibitor for pitting corrosion of stainless steels [2,24,25]. Chromate is a highly effective oxidizing anodic inhibitor that maintains iron in the passive state, prevents breakdown and undermines the passive oxide, which leads to localised corrosion [2,24]. The action of chromate has been extensively studied but the inhibiting mechanisms have not been fully elucidated [2,3,25,26]. It is generally accepted that chromate can passivate metals by forming monoatomic or polyatomic oxide films on the electrode surface. However, its use has been banned due to its toxicity [26]. On the other hand, chromate is commonly used in absorption machines as they are closed systems and has less harm on the environment [2]. Burstein and Ilevbare [25] reported that chromate ion affects pit nucleation by deactivating the sites at which they occur and by reducing the sizes of those that occur. As a result, metastable pits are more difficult to develop from these nucleations and a reduction in the number of metastable pits occurs. This causes a drop in the probability of developing stable

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pits, thus, pitting potential is increased to more noble values [25]. Although the inhibiting effect of chromate on pitting corrosion has been investigated extensively, fewer studies have been contributed to the effect of dichromate as an inhibitor on the critical pitting temperature. In the authors' previous work, [20] the beneficial effect of molybdate ion on increasing critical pitting temperature of DSS 2205 in 0.1 M NaCl has been confirmed. To verify a similar effect of other passivating inhibitor, i.e. dichromate on critical pitting temperature of stainless steel, the present work is proposed. The purpose of this work is to study the beneficial effect of dichromate ion on corrosion behaviour of DSS 2205 in solutions containing NaCl by utilizing microscopic examination, potentiodynamic and potentiostatic polarisations and standard CPT measurements.

## 2. Materials and experimental methods

Experiments were performed on 2205 grade duplex stainless steel sheets with thickness of 30 mm and the following chemical composition (in wt.%): 0.03% C, 0.97% Mn, 0.022% P, 0.0007% S, 0.74% Si, 21.61% Cr, 5.31% Ni, 3.07% Mo, 0.16% Cu, 0.15% N, 0.136% V, 0.064% W, 0.01% Ti and Fe (balance), in agreement with the UNS S31803 (AISI 2205). Samples were prepared in rod and flat types. The rod specimen had 10 mm diameter and 40 mm length with hemispherical end. Orientation of long axis of rod working electrodes was normal to the rolling direction. The immersion depth of working electrode was 12 mm; therefore, the immersion surface area was ca 4 cm<sup>2</sup>. Preparing this shape of samples avoids any crevice corrosion during pitting corrosion measurements. To make sure that the pittings are not affected by waterline attack, the specimen was examined by stereo microscope after each experiment.

Flat samples with small surface area of 0.5 × 0.5 cm<sup>2</sup> were also used in potentiostatic polarisation measurements to accentuate the current fluctuations in passivity region. To prevent crevice corrosion, these specimens were prepassivated in 65% HNO<sub>3</sub> at 75 °C for 1 h. Next, a copper lead was soldered to each of the samples and samples were mounted in epoxy resin. They were then abraded up to 1200 emery paper, washed in acetone solution (ultrasonically), and eventually dried by hot air.

Gill AC potentiostat (ACM Instruments) was employed in a three-electrode cell with a 200 cm<sup>3</sup> capacity. The reference electrode was a saturated calomel electrode (SCE) connected to the cell via a Luggin probe. The capillary tip was close to the working electrode and at about three times of the Luggin probe tip diameter. A platinum wire with a surface area of 2 cm<sup>2</sup> was used as the counter-electrode. All tests related to the pitting potential and CPT evaluations were performed at various temperatures in electrolyte containing 0.1 M NaCl, either without dichromate, or in the presence of 0.0001, 0.001, 0.01 and 0.1 M dichromate, added as Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> salt. The pH of solution was 5.9, measured by Inolab pH meter. In all measurements, the electrolyte in the cell was deaerated for at least 1 h before the experiment while the working electrode was held above the electrolyte. Throughout the experiment, the working electrode was inserted into the solution and the nitrogen sparger was simultaneously raised above the liquid surface. The schematic of the electrochemical cell is shown in Fig. 1. Each test was repeated at least three times to ensure reproducibility.

Potentiodynamic polarisation measurement was carried out at temperatures varying from 25 °C to 75 °C (±1 °C) with a 10 °C increment to obtain the breakdown potential. Before the measurements, open circuit potential (OCP) was obtained for 60 min. The potentiodynamic measurement rate was 0.5 mV s<sup>-1</sup>, starting at 50 mV below OCP up to the anodic potential value at which an abrupt increase in current density occurred. The sudden current increase was either due to extensive pitting corrosion or transpassiv-

ity dissolution. The potential at which the current density exceeded 100 μA/cm<sup>2</sup> was defined as the breakdown potential (*E<sub>b</sub>*) [2]. For the cyclic scans, the potential scan was reversed when the current density as a result of pitting corrosion reached a value of 300 μA/cm<sup>2</sup>.

To investigate the effect of [inhibitor]/[aggressive] ion ratio on CPT, potentiodynamic polarisation measurements were made on solutions containing 0.01 M Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> with 1, 0.1 and 0.01 M NaCl at temperatures varying from 25 to 75 °C.

To study the effect of dichromate as an inhibitor, potentiodynamic polarisation was performed from 200 mV below OCP to 1500 mV above it at 25 °C in concentrated hydrochloric acid i.e. 5 M HCl [27] (simulation of pit solution with pH = -0.9) and 5 M HCl + 0.1 M Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> solutions with sweeping rate of 1 mV s<sup>-1</sup>. Due to the limitation of supply current by potentiostat, no potentiodynamic measurement of alloy in simulated pit solution was carried out at a temperature above 25 °C. All potentiostatic CPT measurements were carried out at applied anodic potential of 600 mV(SCE) and the temperature increased with a rate of no greater than 0.6 °C/min until the current density exceeded to 100 μA/cm<sup>2</sup>. The temperature associated to this current density was chosen as a criterion for CPT assessment [28]. To study the effect of dichromate ions on the passivity current density and metastable pitting, potentiostatic measurements were performed in the anodic potential of 600 mV(SCE) in a solution containing 0.1 M NaCl and 0.1 M NaCl with 0.01 M additions of Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>.

For topographical examination of as-received and pitted specimens, optical microscopy and scanning electron microscope (SEM model Philips XL 20) were used, respectively. The samples were ground and polished to 0.05 μm Alumina slurry finish prior to electrolytic etching in oxalic acid (10%) and KOH (10 N). The etching was done in oxalic acid at 2.5 V for 10 s and then in KOH at 1.5 V for 10 s using a platinum electrode as a cathode and prepared specimen as the anode [29]. Morphology of metastable pits, which were generated by potentiostatic measurements at 600 mV(SCE) in a solution containing 0.1 M NaCl and 0.1 M NaCl plus 0.01 M Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> at 55 °C was examined by SEM.

## 3. Results and discussion

### 3.1. Microstructure evaluation

Fig. 2 presents the microstructure of DSS 2205 with a 51–49% volume fraction of ferrite–austenite. Since the specimen was work hardened, the microstructure phases consisting ferrite and austenite were elongated in the rolling direction. The interface between two phases has been clearly etched, darker and brighter phases, represent ferrite and austenite, respectively [2,3,30].

### 3.2. Potentiodynamic measurements

Potentiodynamic polarisation curves of DSS 2205 alloy in 0.1 M NaCl at different temperatures are shown in Fig. 3 (In order to compare the results here with Fig. 4 the inserted graph shows the polarisation curves in E-i format). First, by increasing the temperature from 25 to 75 °C, the passivity current density increased from 2.6 to 4.5 μA/cm<sup>2</sup>. Moreover, the breakdown potential (potential associated with 100 μA/cm<sup>2</sup> anodic current density) decreased from 1200 mV(SCE) at 25 °C to 400 mV(SCE) at 75 °C. It can be observed that in 0.1 M NaCl, the alloy shows passivity behaviour in the temperature range of 25–45 °C, and increasing the current density at ca 1100 mV(SCE) is due to transpassivity. At 55 °C, increase of current density fluctuations in passivity domain is observed and a transition from transpassivity to pitting corrosion took place (see Fig. 3). Based on the potential value associated to 100 μA/cm<sup>2</sup> as a

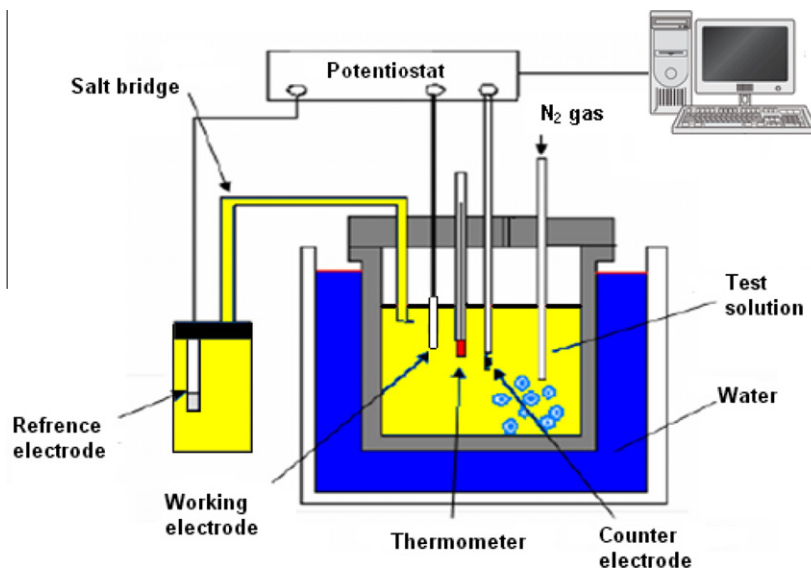


Fig. 1. Schematic of the electrochemical cell used in corrosion tests.

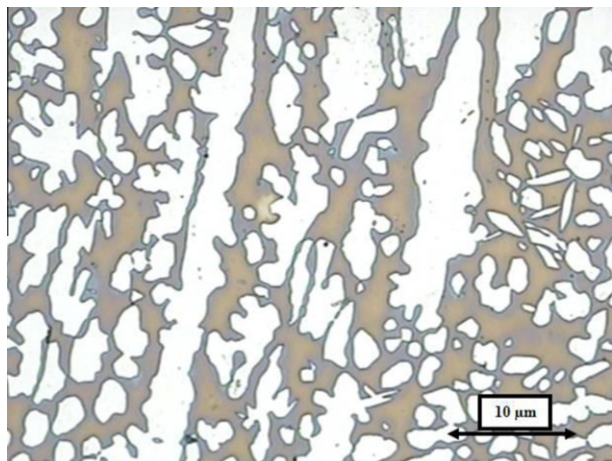


Fig. 2. Optical microscopy of DSS 2205 showing ferrite (dark region) and austenite (bright region) phases.

criterion for the breakdown potential, the pitting potential at 55 °C is ca 970 mV(SCE). By increasing the temperature, the passivity domain (from OCP to breakdown potential) is decreased from 1300 mV(SCE) at 45 °C to 690 mV(SCE) at 65 °C and 560 mV(SCE) at 75 °C. In the present study, the breakdown potential of 490 mV(SCE) at 65 °C was obtained in 0.1 M NaCl. A value of 400 mV(SCE) has been reported previously for breakdown potential at 60 °C in 3.5% NaCl [6]. This confirms that the breakdown potential depends on both temperature and the chloride concentration. In summary, based on potentiodynamic measurements at various temperatures, shown in Fig. 3 a transition from transpassivity to pitting corrosion occurred between 45 and 55 °C in 0.1 M NaCl solution.

Potentiodynamic results of the alloy in 0.1 M NaCl plus 0.0001, 0.001, 0.01 and 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  at different temperatures are shown in Fig. 4. Generally, the influence of adding dichromate ions on breakdown potential in the temperature range of 25–55 °C was insignificant. In the temperature range of 25–45 °C, transpassivity occurred at high potentials and no pitting was observed. By increasing the temperature to 55 °C, pitting occurred in a solution containing 0.0001 M  $\text{Cr}_2\text{O}_7^{2-}$ . However, no significant decrease in breakdown potential could be noticed. Further increase of the temperature re-

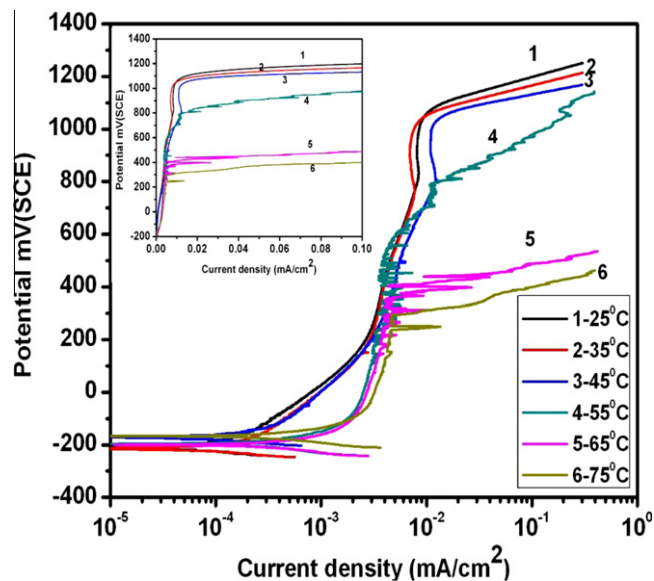


Fig. 3. Potentiodynamic polarisation curves of DSS 2205 in 0.1 M NaCl at different temperatures. Scan rate was 0.5 mV/s. To compare the results here with Fig. 4. The inserted graph shows the polarisation curves in E-i format.

sulted in a significant decrease in breakdown potential due to extensive pitting occurrence. By adding 0.001 M dichromate, pitting behaviour changed to transpassivity at 55 °C. Fig. 5 shows the cyclic potentiodynamic polarisation curve of DSS 2205 in 0.1 M NaCl containing 0.0001 and 0.001 M  $\text{Cr}_2\text{O}_7^{2-}$  at 55 °C. Clearly with  $10^{-4}$  M inhibitor, the alloy exhibits a hysteresis loop at 55 °C, indicating that repassivation of existing pits are more difficult when the potential is swept toward the negative direction. However, by adding the inhibitors, forward and backward potentiodynamic scans are the same, indicating a transpassivity characteristic of passivation breakdown [3]. Rising  $\text{Cr}_2\text{O}_7^{2-}$  concentration to 0.01 M caused even more improvement of pitting potential especially at 65 °C. This can be seen more clearly in Fig. 6 where the breakdown potential of DSS 2205 obtained by Fig. 4 has been plotted against the temperature. By Further increasing the dichromate concentration to 0.1 M, the breakdown potential increased noticeably and reached

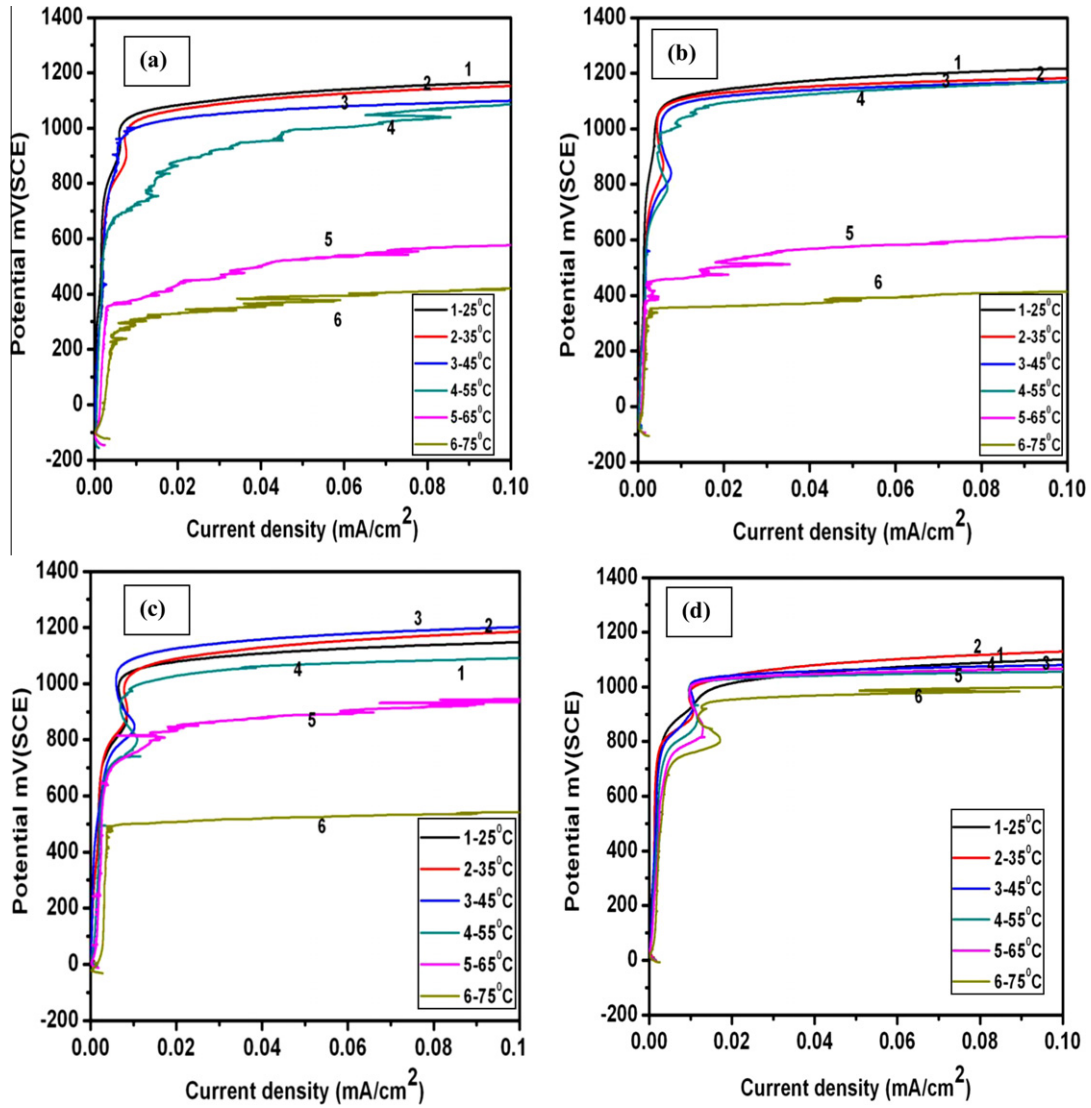


Fig. 4. Potentiodynamic polarisation curves of DSS 2205 in 0.1 M NaCl with (a) 0.0001, (b) 0.001, (c) 0.01, and (d) 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  at different temperatures. Scan rate was 0.5 mV/s.

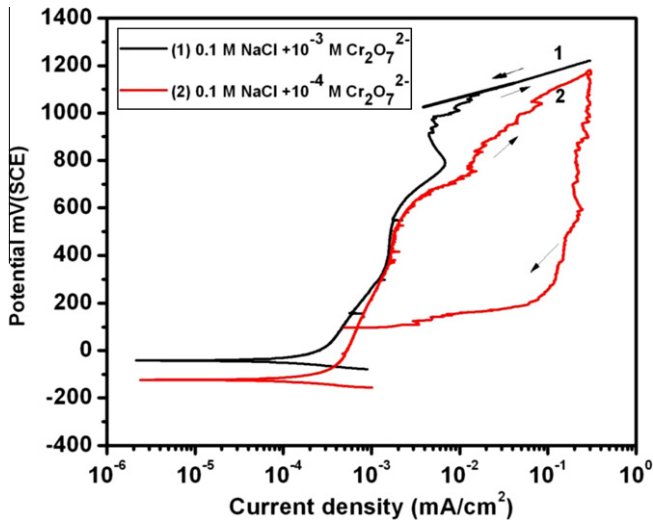


Fig. 5. Cyclic potentiodynamic polarisation curves of DSS 2205 in 0.1 M NaCl +  $10^{-3}$  M  $\text{Cr}_2\text{O}_7^{2-}$  and 0.1 M NaCl +  $10^{-4}$  M  $\text{Cr}_2\text{O}_7^{2-}$  at 55 °C.

transpassivity even at 75 °C. See Fig. 6. This means that the pitting corrosion did not occur in 0.1 M NaCl + 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  even at the highest recorded temperature, 75 °C.

A logarithmic relationship exists between the pitting potential ( $E_p$ ) and the ratio between the inhibitive and aggressive ions, as follows [31]:

$$E_p = K + n \log \left[ \frac{C_A^{2-}}{C_x^-} \right] \quad (1)$$

Where  $E_p$  is the pitting potential,  $C_A^{2-}$  is the concentration of inhibitive species and  $C_x^-$  is the concentration of aggressive species,  $K$  and  $n$  are constants. Since the concentration of aggressive species is constant (0.1 M NaCl), a linear relationship should exist between  $E_p$  and logarithm of inhibitor concentration,  $\log C_A^{2-}$ . As an example, Fig. 7 shows the correlation between pitting potential and dichromate concentration at 65 °C. According to Eq. (1), the following relation can be extracted;

$$E_p = 1070 + 180.3 \log \left[ \frac{C_{\text{Cr}_2\text{O}_7^{2-}}}{[0.1]} \right] \text{ mV(SCE)} \quad (2)$$

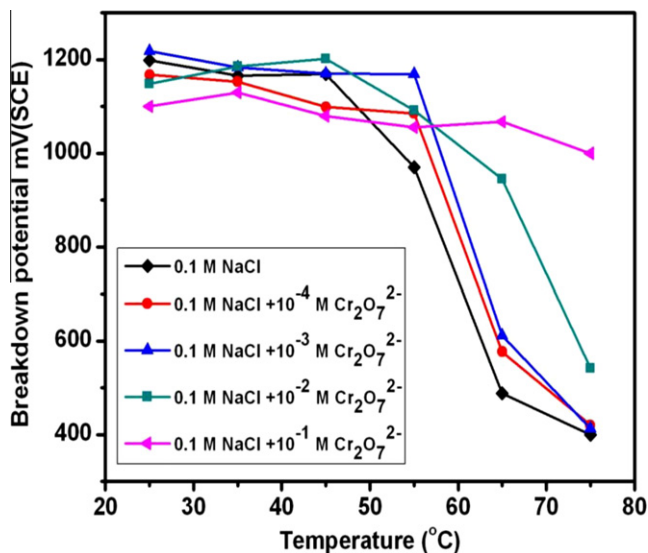


Fig. 6. Evaluation of breakdown potential for 2205 DSS based on the results in Fig. 4. A  $100 \mu\text{A}/\text{cm}^2$  was chosen.

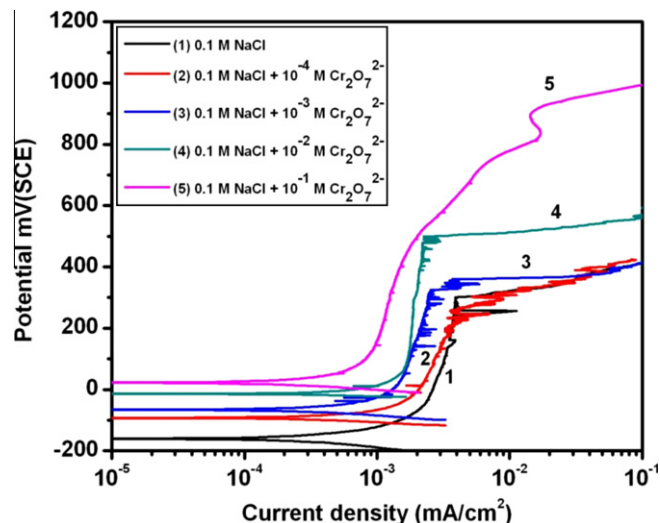
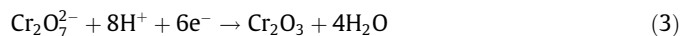


Fig. 8. Potentiodynamic polarisation curves of DSS 2205 in 0.1 M NaCl and 0.1 M NaCl plus 0.0001, 0.001, 0.01 and 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  at  $75^\circ\text{C}$ . Scan rate was 0.5 mV/s.

trochemical reaction has a reversible equilibrium potential ( $E_{\text{eq}}$ ), which depends on the pH and dichromate concentration (Eq. (4)). As a result, the free corrosion potential is more positive in the presence of inhibitor.



$$E_{\text{eq}} = 1.168 - 0.079\text{pH} + 0.0096 \log[\text{Cr}_2\text{O}_7^{2-}]V_{\text{SHE}} \quad (4)$$

Increase in the pitting potential in the presence of inhibitor indicates that  $\text{Cr}_2\text{O}_7^{2-}$  is very effective in retarding the onset of stable pitting [25].

Results of this study reveal that the highest passivity current density is associated with the 0.1 M NaCl solution and adding  $\text{Cr}_2\text{O}_7^{2-}$  decreases the passivity current density from 4.5 to  $2 \mu\text{A}/\text{cm}^2$ . In summary, at room temperature up to  $65^\circ\text{C}$ , the optimal  $\text{Cr}_2\text{O}_7^{2-}$  concentration as satisfactory inhibitor is ca 0.01 M whereas at temperatures higher than  $65^\circ\text{C}$ , the optimum  $\text{Cr}_2\text{O}_7^{2-}$  concentration is 0.1 M. Generally, the beneficial effect of inhibitor is more enhanced at high temperature.

In order to investigate the effect of  $[\text{inhibitor}]/[\text{Cl}^-]$  ratio on critical pitting temperature, potentiodynamic polarisations at various temperatures were carried out in solutions of several  $[\text{inhibitor}]/[\text{Cl}^-]$  ratios. Fig. 9 represents the results of potentiodynamic polarisations at various  $[\text{inhibitor}]/[\text{Cl}^-]$  ratios with constant 0.01 M dichromate concentration. It is evident that in solution containing 0.01 M dichromate and 1 M NaCl pitting corrosion takes place at  $55^\circ\text{C}$  with a pitting potential of 550 mV (see Fig. 9a). By comparing CPT results of this solution with that of the solution of the same concentration of dichromate but ten times lower chloride concentration (0.1 M NaCl) (Fig. 9b) it can be seen that the CPT has moved up  $10^\circ\text{C}$ . In solution of 0.01 M dichromate and 0.1 M NaCl the alloy suffered from pitting corrosion at  $65^\circ\text{C}$  with a pitting potential value of 935 mV. Interesting results were observed in solution of 0.01 M dichromate and 0.01 M NaCl solution (Fig. 9c). Potentiodynamic polarisation of alloy at this solution at various temperatures showed a wide range of passivity and no pitting corrosion upto  $75^\circ\text{C}$ . The alloy was eventually dissolved by transpassivity at quite high anodic potential. Similar results were also observed in solution of 0.1 M dichromate and 0.1 M NaCl, in which no pitting corrosion was detected up to  $75^\circ\text{C}$  in potentiodynamic measurement (see Fig. 4d). In Fig. 9c by raising the temperature from 25 to  $75^\circ\text{C}$ , transpassive potential slightly decreased

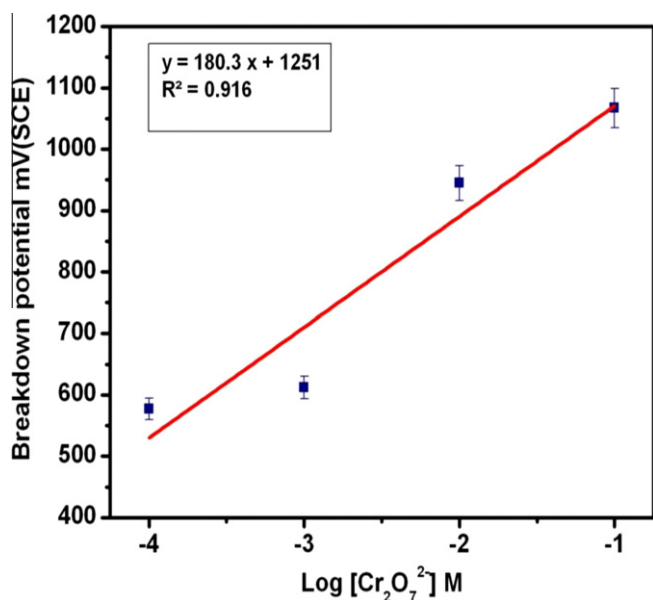


Fig. 7. Correlation between pitting potential and dichromate concentration at  $65^\circ\text{C}$ .

Increasing the breakdown potential due to adding  $\text{Cr}_2\text{O}_7^{2-}$  can be associated with reducing the numbers and the magnitude of metastable pitting transients on 2205 DSS alloy surface. This means that dichromate ions block the active sites on the surface and significantly decrease metastable pitting current transients [25]. The effectiveness of dichromate as an inhibitor lies in the ability to form passive films, which is similar to those formed on Fe-Cr alloys and stainless steels [26].

To clarify the influence of adding dichromate ion on passive current density, potentiodynamic polarisation curve of DSS 2205 in 0.1 M NaCl in the presence and absence of different concentrations of  $\text{Cr}_2\text{O}_7^{2-}$  at  $75^\circ\text{C}$  has been plotted and shown in Fig. 8. Generally by increasing  $\text{Cr}_2\text{O}_7^{2-}$  concentration, corrosion potential and pitting potential increase to more noble values. Moreover, the passive current density decreases.

In the presence of inhibitor, cathodic reaction is likely to be due to the reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}_2\text{O}_3$  according to Eq. (3). This elec-

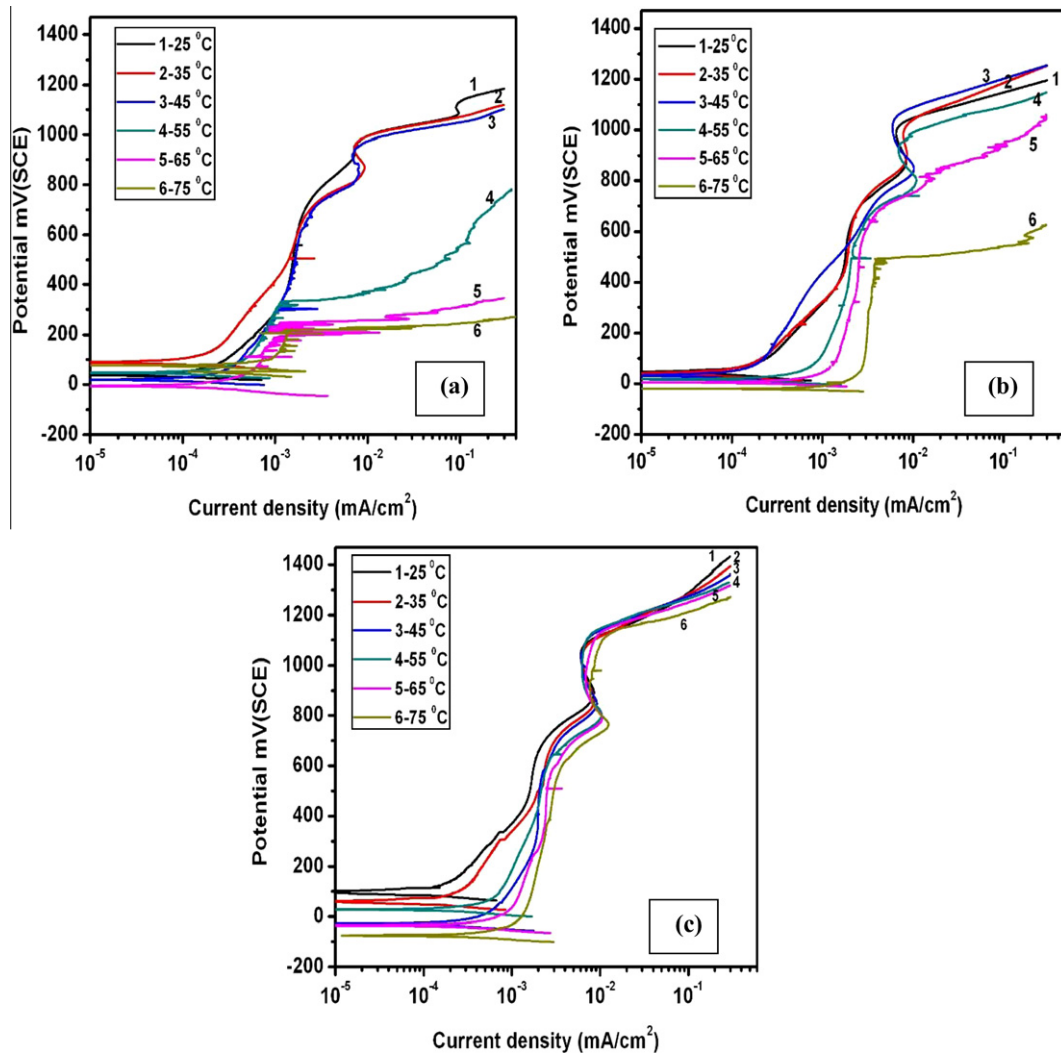


Fig. 9. Potentiodynamic polarisation curves of DSS 2205 in 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  with (a) 1, (b) 0.1, and (c) 0.01 M NaCl at different temperatures. Scan rate was 0.5 mV/s.

and passive current density increased. The overall obtained information from the polarisation curves is shown in Fig. 10 where the variation of breakdown potential with the temperature is illustrated for solutions with different NaCl concentrations. At temperatures of more than 45 °C in all three solutions at constant dichromate concentration (0.01 M) when the concentration of chloride increased the pitting potential decreased. This behaviour is mentioned by many investigators [32,33,21]. Table 1 shows the occurrence of pitting corrosion in solutions of various [inhibitor]/[Cl<sup>-</sup>] ratios at various temperatures. It is evident that CPT directly depends on the ratio of inhibitor to aggressive ion concentration. Pitting corrosion occurred for solutions with a ratio of less than one of inhibitor to aggressive ion. However, when this ratio was increased to one (solution of 0.01 M dichromate and 0.01 M NaCl) no pitting was observed upto 75 °C (the highest temperature in these experiments). This means that the beneficial effect of dichromate on CPT is declined when the concentration of aggressive anion (here Cl<sup>-</sup>) is increased in solution. The counter effect of inhibitor action with chloride concentration was first mentioned by Leckie and Uhlig [21]. They proposed that there is a competition between inhibitor and chloride anions for adsorption on the passive surface. When a sufficiently high surface concentration of chloride is presented, oxygen which makes up the passive film is displaced locally by Cl<sup>-</sup> and, therefore, passivity is destroyed and pitting is initiated. At the presence of inhibitor, inhibitor anions

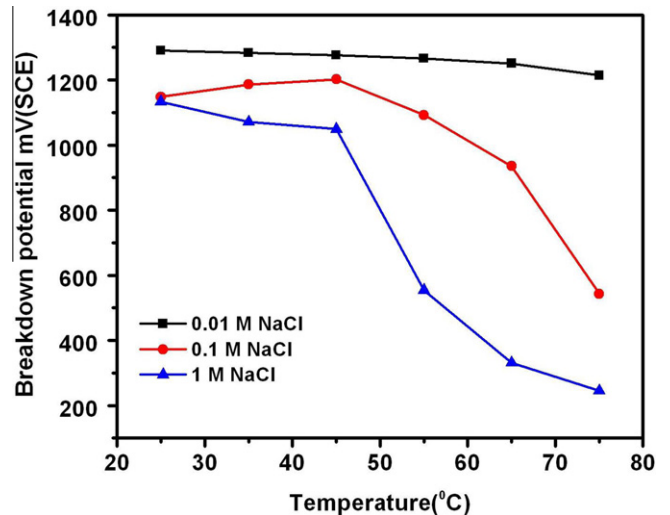


Fig. 10. Evaluation of breakdown potential for DSS 2205 in 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  with different NaCl concentration based on the results in Fig. 9. A 100  $\mu\text{A}/\text{cm}^2$  was chosen.

tend to adsorb on surface and displace the adsorbed chloride ions. Therefore, pitting is postponed. Leckie and Uhlig [21] proposed

**Table 1**

The occurrence of pitting corrosion in solutions of various  $\frac{[Cr_2O_7^{2-}]_{IM}}{[NaCl]_{IM}}$  ratios at constant dichromate concentration of 0.01 M with temperature.

$\frac{[Cr_2O_7^{2-}]_{IM}}{[NaCl]_{IM}}$	25 °C	35 °C	45 °C	55 °C	65 °C	75 °C
0.01	No	No	No	Yes	Yes	Yes
0.1	No	No	No	No	Yes	Yes
1	No	No	No	No	No	No

that a minimum concentration of inhibitor anion is needed for inhibiting the pitting corrosion in chloride containing solution. The greater the chloride concentration, the greater the inhibitor concentration required to prevent pitting corrosion [21].

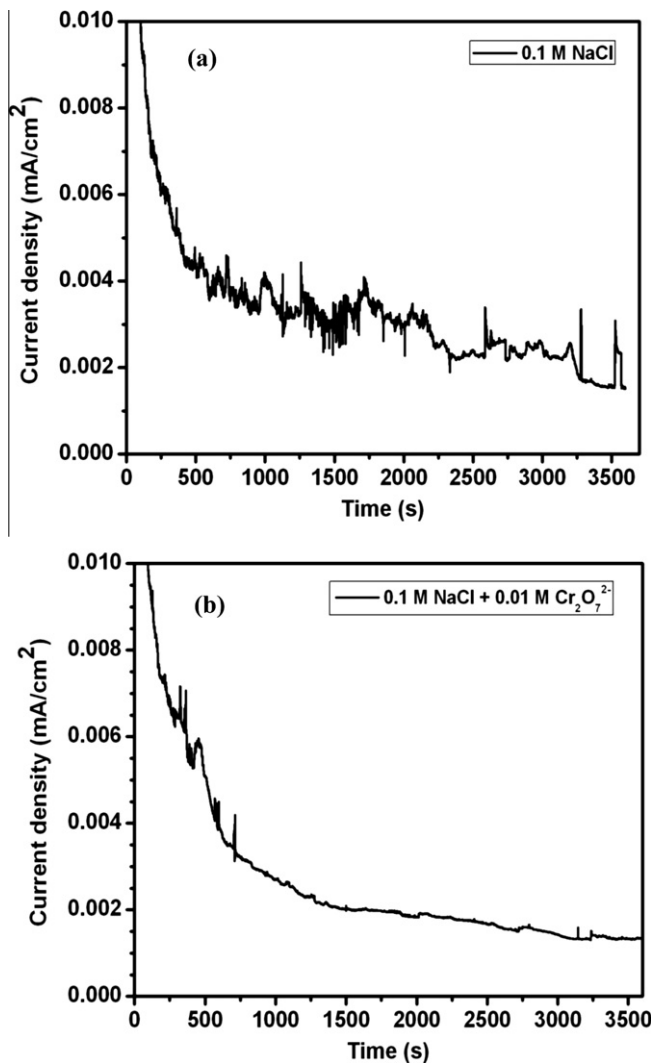
The opposition effect of inhibitor and aggressive anion on pitting corrosion has also been proposed by Galvele [34–38]. In a series of papers [34–38] based on the acidification of pit solution as a result of metal cation hydrolysis, Galvele introduced a critical pit stability criterion, which is defined as the product of pit current density ( $i$ ) and pit depth ( $x$ ). This product depends on alloy and electrolyte composition. He proposed that a sharp rise of  $H^+$  activity happens when the pit stability criterion reaches its critical value. He suggested that pitting potential is the sum of four components [36]:

$$E_p = E_c^* + \eta + E_{inh} + \Phi \quad (5)$$

Where  $E_c^*$  is the corrosion potential of metals in acidified pit-like solution,  $\eta$  is the anodic polarisation necessary to draw enough current through the pit to provide the critical  $x \cdot i$  in the absence of inhibitor,  $E_{inh}$  is the extra potential required when inhibitors are presented and  $\Phi$  is the electrical potential inside the pit when ion migration is considered. According to Galvele model [36,38] by adding passivating inhibitor, such as dichromate in chloride containing solution, inhibitor ions migrate into pit cavity and as a result, all parameters mentioned in Eq. (5) may change. The inhibitor's main influence is increasing pitting potential by increasing the extra potential necessary for reaching the critical value for pit stability criterion [36,38]. But, at the presence of inhibitor in a constant applied potential, the potential is not adequate to cause pitting corrosion. Therefore, in order to provide the driving force for further metal dissolution inside the pit and to reach the critical value for  $i \cdot x$ , it is necessary to raise the temperature, which leads to higher CPT.

### 3.3. Potentiostatic polarisation measurements

Fig. 11 shows current transient obtained from the potentiostatic polarisation of specimen in 0.1 M NaCl (Fig. 11a) and 0.1 M NaCl + 0.1 M  $Cr_2O_7^{2-}$  (Fig. 11b) at 0.6 V(SCE) for 3600 s. As it can be observed, in both solutions, the background current decreases with time. Furthermore, there are impermanent current spikes above the mean current, which are either nucleation or metastable pitting events [25,39]. In both solutions, the background current starts to fall abruptly during the first 500 s and then more gradually. It is evident that in the presence of dichromate, the fluctuation of events and peak heights are decreased particularly after approximately 500 s. This is similar to the previously reported results on the inhibition of pitting corrosion of stainless steels AISI 304 and AISI 316 by chromate ions in acidified chloride solution [25]. Statistical analysis of Burstein and Ilevbare [25] on potentiostatic experiments showed that in AISI 304 and AISI 316 the average frequency of events in all times was decreased in the presence of inhibitor. However, height distribution of nucleations in inhibited and pure solution was almost equal in early stages of the experiment and by passing time it decreased to lower values in the presence of inhibitor [25]. Noticeably, after 1500 s, the current density in



**Fig. 11.** Potentiostatic polarisation results of 2205 DSS by applying 600 mV(SCE) (a) 0.1 M NaCl and (b) 0.1 M NaCl + 0.01 M  $Cr_2O_7^{2-}$ .

0.1 M NaCl without inhibitor was about  $2.88 \mu A/cm^2$ , which is more than the solution containing 0.01 M  $Cr_2O_7^{2-}$  ( $1.98 \mu A/cm^2$ ). In summary, potentiostatic polarisation measurements confirm the potentiodynamic results on the beneficial influence of adding dichromate ions on improving pitting corrosion resistance by decreasing passivity current density and the occurrence of metastable pit events.

### 3.4. Potentiostatic CPT measurements

Fig. 12 represents the results on assessment of CPT in DSS 2205 with potentiostatic measurement by applying the 600 mV(SCE) anodic potential and gradually increasing the temperature. Considering the  $100 \mu A/cm^2$  current density as a criterion for CPT evaluation, it can be seen that adding 0.0001, 0.001, and 0.01 M  $Cr_2O_7^{2-}$  increased CPT about 0, 5, and 12 °C, respectively (from 60 °C in 0.1 M NaCl to 72 °C in 0.1 M NaCl + 0.01 M  $Cr_2O_7^{2-}$ ). Significantly low  $Cr_2O_7^{2-}$  concentration in  $Cl^-$  containing solutions exposed a negligible positive effect on CPT. However, high enough  $Cr_2O_7^{2-}$  concentration, more than 0.01 M, demonstrated a great inhibiting effect by increasing CPT values. Noticeably, by adding 0.1 M  $Cr_2O_7^{2-}$  no abrupt rise in current was observed up to 87 °C (maximum temperature obtained by water bath) indicating no pitting corrosion occurred in the presence of 0.1 M dichromate until 87 °C.

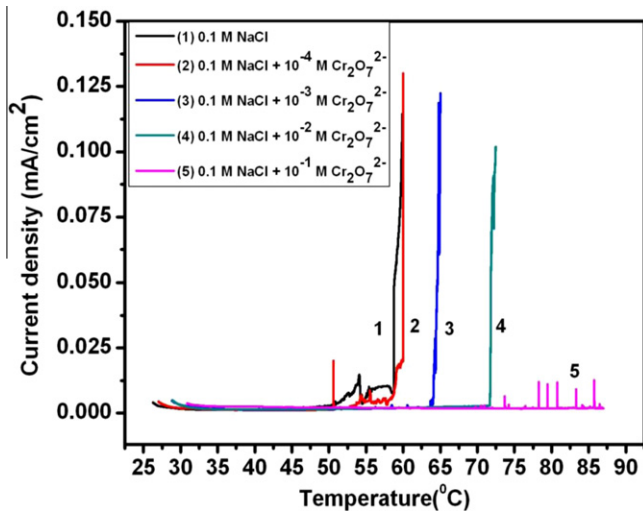


Fig. 12. Evaluation of CPT in 2205 DSS with potentiostatic measurement at anodic potential of 600 mV(SCE) and temperature increasing rate 0.6 °C/min.

The value of CPT measured by potentiostatic method for DSS 2205 alloy in 0.1 M NaCl solution is 59 °C. Similar CPT value for the same alloy in 1 M NaCl solution was also reported by Deng et al. [40]. The independency of austenitic stainless steel CPT of chloride concentration was also mentioned by Laycock and Qvarfort [33,41].

### 3.5. Simulated pit solution investigation and inhibiting mechanisms

Inhibiting effect of chromate has been extensively studied before [2,14,25]. Burstein and Ilevbare showed that chromate affects pit nucleation by deactivating the sites at which they occur and by reducing the sizes of those that occur [25]. According to the possible reactions given in Eq. (3) reduction products are believed to be deposited on the metal surface especially at the sites of inclusions. This suggests that pit initiation at weak sites on the surface will be followed by fast repassivation [25,42]. Since dichromate ions block the reactive sites, the  $\text{Cl}^-$  ions are not able to get to the inclusions to activate these sites [25]. A further explanation for the inhibiting ability of  $\text{Na}_2\text{Cr}_2\text{O}_7$  is that the reduction of each mole of dichromate ions consumes eight moles of protons, therefore, local pH is increased, necessary aggressiveness for pit development is diminished and pitting growth is inhibited [25,42].

It is known that CPT is related to the transition from metastable to stable pit growth. According to the mechanism proposed by Salinas-Bravo and Newman [27], it can be assumed that all stable pits must develop and maintain an anodic salt. Additionally, there is a critical current density for passivation in the saturated salt environment of the pit nucleus,  $i_{\text{crit}}$  which increases with the temperature. There is also a limiting current density,  $i_L$  given by the saturation concentration of metal ions,  $C_S$  and Fick's first law, which increase more gradually with the temperature than  $i_{\text{crit}}$  [41].

$$i_L = \frac{nFD C_S}{\delta} \quad (6)$$

Where  $C_S$  is the saturation concentration of salt,  $\delta$  the pit radius,  $D$  the diffusivity of metal cation,  $n$  the dissolution valence and  $F$  the Faraday constant. The CPT corresponds to the temperature at which  $i_{\text{crit}} = i_L$  [27]. Below this temperature the alloy cannot generate enough anodic current density ( $i_{\text{crit}}$ ) to maintain pit stability. Therefore, increasing the temperature (meaning higher CPT) or applying higher anodic potential [36] may compensate the lack of anodic current density within the pit cavity.

To simulate the pit chemistry and study the influence of inhibitor, potentiodynamic polarisation measurements were carried out in the presence and absence of dichromate ions. Fig. 13 depicts the potentiodynamic polarisation curves in deaerated 5 M HCl (representing of synthetic pit solution [27]) and 5 M HCl + 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  at 25 °C. As it was mentioned above, at the presence of dichromate ions, a new cathodic reaction exists, Eq. (3). This cathodic reaction comes across the anodic branch at three points; in active, transition from active to passive and passive regions leading to three different corrosion potentials. It is also obvious that in the presence of dichromate ions corrosion potential has been increased while critical current density has been decreased. Measurement of critical current density of alloy in 5 M HCl at 25 °C revealed that the dichromate has had a large effect on  $i_{\text{crit}}$  and dropped it from 60 to 18 mA/cm<sup>2</sup> (see Fig. 13). Assuming dichromate has a similar effect on pit kinetics at higher temperatures by means of decreasing  $i_{\text{crit}}$ , the required current density for pit stability has to be produced by increasing the temperature (meaning the alloy shows higher CPT at the presence of dichromate).

Another explanation for positive effect of dichromate on CPT is that the presence of dichromate ions apparently deactivates the anodic kinetics [25] such that a higher potential is required to reach a given anodic current density within the simulated pit environment (see Fig. 13). Consequently, in the absence of any other effect, a higher potential is required to reach the critical value of  $i \cdot x$  for pit stability, which was proposed by Galvele [34–38]. Consequently, for the occurrence of pitting at the presence of dichromate, the applied potential or solution the temperature has to be raised.

### 3.6. Pit observation

Fig. 14 reveals an example of metastable and stable pit morphology of DSS 2205 in 0.1 M NaCl and 0.1 M NaCl + 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  after applying an anodic potential of 700 mV(SCE) in a potentiostatic polarisation at 55 °C. A few metastable pits were observed in austenite phase and austenite–ferrite interface, which is clearer in Fig. 14. It is reported [1] that pitting resistance equivalent number (PREN) for austenite gives lower values than that of ferrite. As a consequence, the metastable pits are nucleated in austenite. Again, a cluster of pitting cavities are observed in 0.1 M NaCl

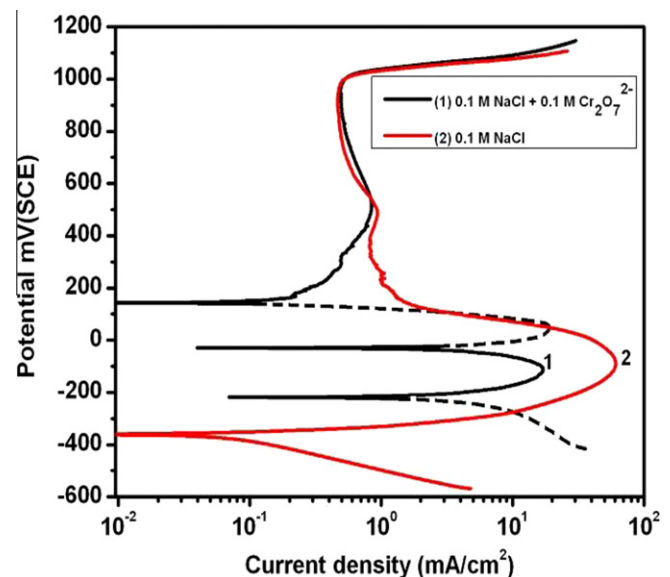
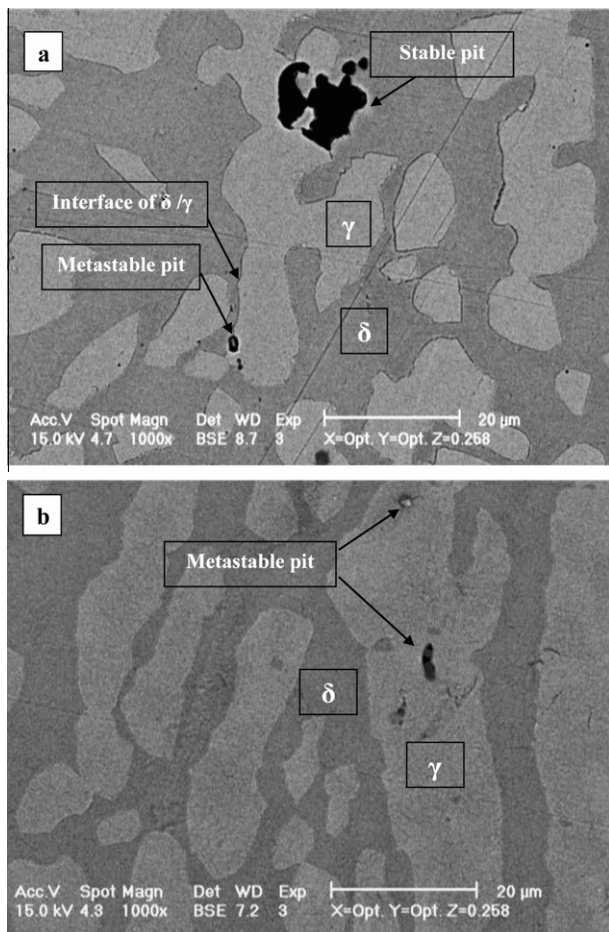


Fig. 13. Potentiodynamic polarisation curves of DSS 2205 in 5 M HCl and 5 M HCl plus 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  at 25 °C. Scan rate was 1 mV/s. Dashed line shows net cathodic current density in 5 M HCl plus 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  solution.





**Fig. 14.** Metastable and stable pit morphology of DSS 2205 (a) in 0.1 M NaCl after 700 mV(SCE) potentiostatic polarisation at 55 °C (b) in 0.1 M NaCl + 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  after 700 mV(SCE) potentiostatic polarisation at 55 °C.

solution. It seems that the pitting initiated in the boundary regions between austenite and ferrite, which are probably the weakest points on the surface [1] and mainly propagated into austenite phase. This has been also reported previously [43] and recently by Deng et al. [1]. The reason may be associated to chromium depletion in austenite–ferrite interface and consequently the lower chromium content in austenite compared to ferrite phase or probably higher density of inclusions in this area [20]. In comparison to specimens without inhibitor, it seems metastable pits could not become stable.

#### 4. Conclusions

In this research, influence of various concentrations of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ion, as an inorganic inhibitor, on the pitting potential and CPT of DSS2205 in NaCl solution has been investigated. The results could be summarized as follows;

1. Potentiostatic CPT measurements showed that in the presence of 0.0001 and 0.001 M dichromate, CPT increased 0 and 5 °C, respectively. Furthermore, adding 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  raised CPT by 12 °C and in solution containing 0.1 M dichromate no pitting was observed up to 87 °C.
2. Potentiodynamic polarisation results showed that the pitting potential increases by the addition of dichromate in a constant NaCl concentration of 0.1 M. Furthermore in a constant  $\text{Cr}_2\text{O}_7^{2-}$  concentration of 0.01 M the pitting potential decreased by increasing the NaCl concentration.

3. Critical pitting temperature depends on [inhibitor]/[aggressive] ion ratio. In a ratio of [dichromate]/[chloride] equal to one in solutions containing 0.01 M NaCl + 0.01 M  $\text{Cr}_2\text{O}_7^{2-}$  and 0.1 M NaCl + 0.1 M  $\text{Cr}_2\text{O}_7^{2-}$  no pitting was observed up to 75 °C.
4. Morphological studies of pits revealed the presence of propagated stable pits in austenite phase and austenite–ferrite interface in solution without dichromate. This was associated with the lower pitting resistance equivalent number (PREN) of austenite compared to ferrite phase, chromium depletion in austenite–ferrite interface and probably higher density of inclusions in this area. At the same temperature, a few metastable pits could be observed on DSS 2205 in solution containing inhibitor.

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