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ORIGINAL PAPER

Role of alloyed silicon and some inorganic inhibitors in the inhibition of meta-stable and stable pitting of Al in perchlorate solutions

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Abstract The study of both meta-stable and stable pitting events on the surface of pure Al and three Al–Si alloys, namely (Al + 6%Si), (Al + 12%Si) and (Al + 18%Si) alloys, was carried out in deaerated neutral $NaClO_4$ solutions of various concentrations (10^{-4}–10^{-2} M). Measurements were carried out under the effect of various experimental conditions using potentiodynamic anodic polarization and potentiostatic techniques. The results presented below showed that meta-stable pits (appeared as oscillations in current) form at potentials close to the pitting potential (E_{pit}) and during the induction time for stable pit formation. Various factors affecting the rate of meta-stable and stable pits were studied. The presence of Si as an alloying element in Al reduces the rate of formation of meta-stable pits, corresponding to a reduction in the probability of developing stable pits, and an increase in the pitting potential results. The inhibitive effects of chromate, silicate, molybdate and tungstate on pitting corrosion in Al were also studied. Results obtained showed that these known inhibitors retard both meta-stable and stable pitting events. This makes attainment of stable pit growth more difficult in presence of these inhibitors.

Keywords Pitting corrosion · Meta-stable and stable pits · Al · Al–Si alloys · Sodium perchlorate solutions · Inorganic inhibitors

1 Introduction

Pure aluminium usually experiences low rates of corrosion as it is covered with a protective oxide coating [1]. This coating is amphoteric and may be dissolved by acidic or basic media [2]. However, the oxide coating, even at the extremes of the pH range, is not totally removed but is thinned and regenerated by oxidation of the underlying metal [3]. In some instances, the underlying metal may be exposed by the local formation of flaws within the oxide [4]. When the underlying metal is exposed in a controlled manner it reacts very rapidly to regenerate the oxide [5]. However, in the presence of some ions, most notably chloride ions, the flaws within the oxide coating are unable to be repaired immediately [6]. It is thought that these ''pit promoting'' ions interfere with the oxide formation chemistry preventing local passivation of the metal [7]. Metal dissolution then continues beneath the fracture and a corrosion pit develops. As the aluminium dissolves, hydrolysis occurs producing hydrogen ions that lower the pH within the pit [8]. If this continues, a point may be reached where the internal pH within the pit is low enough to make aluminium oxide formation unfavourable [2]. At this point the pit can no longer passivate and becomes a stable pit.

However, many years ago several researchers observed oscillations of anodic current at potentials close to the

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pitting potential for different metals and alloys in chloride solutions [9]. The occurrence of these oscillations was explained by the consecutive formation and repassivation of microsize pits (meta-stable pits). The meta-stable pits are very small in size and grow and repassivate in less than a few seconds. However, until the last decade no studies of these micropits were performed in detail. It was expected that the knowledge of the processes occurring during the formation and repassivation of the meta-stable pits would be helpful in understanding the processes which determine the stable growth of pits. The most important issues in the meta-stable pit studies are the processes leading to the formation of meta-stable pits and the electrochemical factor or factors that influence the transition of meta-stable to stable pits. When the meta-stable pits occur the current increases as the pits nucleate and begin to grow, and then decreases after a short time. There are many studies of meta-stable pits on steels [10–13] but few on aluminum [14]. Most of the studies that have been carried out of the effect of inhibitors on pitting corrosion of metals and alloys have concentrated on stable pitting, which is usually quantified or described by the pitting potential. The objective of the present work is to study the effect of alloyed silicon and some inorganic inhibitors as chromate, silicate, molybdate and tungstae (in the form of CrO_4^{2-}, SiO_3^{2-}, $MoO_4^{2-}$and WO_4^{2-}, respectively), on meta-stable and stable pitting of Al in aggressive perchlorate solutions.

2 Experimental

The working electrodes employed in the present work were made of very pure Al (99.999% Koch Kight Laboratories, Colnbrook Buckes, UK), (Al + 6 wt%Si) and (Al + 12 wt%Si) and (Al + 18 wt%Si) alloys. The four electrodes, namely pure Al and the three Al–Si alloys, were used in the as-received condition. The three Al–Si alloys were provided from the Egyptian Aluminium Company (EAC). The investigated electrodes were cut as cylindrical rods, welded with Cu-wire for electrical connection and mounted into glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of (0.50 cm^2) geometric area for the working electrode, to contact the test solution. Prior to each experiment, the surface pretreatment of the working electrode was performed by mechanical polishing (using a polishing machine model POLIMENT I, BUEHLER POLISHER) of the electrode surface with successive grades of emery papers down to 1,200 grit up to a mirror finish. The electrode was then, rinsed with acetone, distilled water, and finally dipped in the electrolytic cell.

The experiments were performed in a 100 mL volume Pyrex glass cell using Pt wire and a saturated calomel electrode (SCE) as auxiliary and reference electrodes, respectively. All potentials given in this paper are referred to this reference electrode. The experiments were carried out in different concentrations (10^{-4}–10^{-2} M) of $NaClO_4$ solutions. Some experiments were performed in 0.005 M perchlorate solutions containing 0.001 M of K_2CrO_4, Na_2SiO_3, Na_2MoO_4 and Na_2WO_4, as inorganic inhibitors. All solutions were freshly prepared from analytical grade chemical reagents using doubly distilled water and were used without further purification. All solutions were sparged with Ar gas for 30 min prior to use. Ar bubbling was stopped to prevent convection effects and the argon blanket was maintained over the solution throughout the experiment. The working electrode was then immediately immersed in the test solution without or with the desired concentration of the investigated inhibitors. For each run, a freshly prepared solution as well as a cleaned set of electrodes were used. Each run was carried out in deaerated stagnant solution at the required temperature (± 1 °C), using water thermostat.

The potentiodynamic anodic current–potential curves were recorded for all tested Al samples by changing the electrode potential automatically from −0.40 V (SCE), more positive than E_{corr} under all experimental conditions, up to anodic potentials exceeding the respective pitting potentials with the required scanning rate. The potentiostatic measurements were carried out at a given step anodic potential ($E_{s,a}$) at which the current transient was recorded. A Potentiostat/Galvanostat (EG&G model 273) and a personal computer were used. M352 corrosion software from EG&G Princeton Applied Research was used for the potentiodynamic polarization and the potentiostatic j/t measurements.

3 Results and discussion

3.1 Potentiodynamic anodic polarization measurements

3.1.1 Effect of perchlorate concentration

The influence of perchlorate concentration (10^{-4}–10^{-2} M) on the potentiodynamic anodic polarization behaviour of pure Al and the three Al–Si alloys has been studied. Some of the results obtained are collected in Fig. 1a–h. In all cases, potentials were swept starting from −0.40 V vs SCE (more positive than the corrosion potential of each electrode under various experimental conditions) in the anodic direction at a scan rate of 1.0 mV s^{-1} at 25 °C. Before each polarization experiment, the electrode was allowed to corrode freely for a period of 1 h. After this time a steady state open circuit potential, OCP, corresponding to the

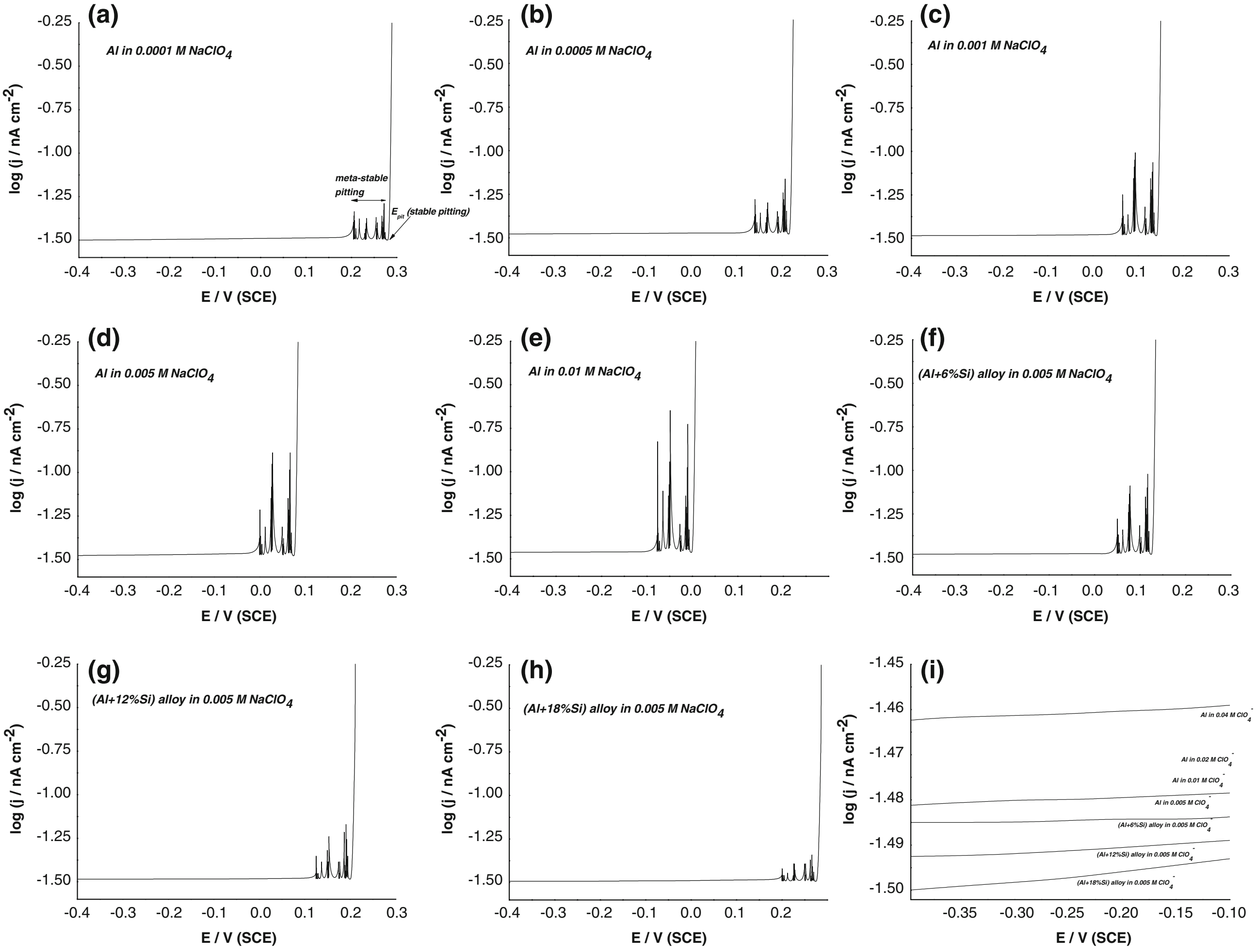

Fig. 1 Potentiodynamic anodic polarization curves recorded for pure Al in $NaClO_4$ solution of various concentrations (10^{-4}–10^{-2} M) (**a**–**e**), for (Al + 6%Si), (Al + 12%Si), and (Al + 18%Si) alloys in 0.005 M $NaClO_4$ solution (**f**–**h**) and for a comparison of the passive region for the four tested Al samples as a function of ClO_4^- concentration (**i**). Measurements were carried out at a scan rate of 1.0 mV s^{-1} and at 25 °C

corrosion potential (E_{corr}) of the working electrode, was obtained. The potential sweep was started from −0.40 V (SCE) in order to avoid the problem of the reduction of perchlorate ions to Cl^- ions [15].[1] It is obvious from Fig. 1a–h that passivity persists as the potential is increased to a value exceeding a certain critical potential value, known as the pitting potential (E_{pit}). The relative insensitivity of current to increasing potential (characteristic of the passive region) changes abruptly as passivity breaks down at E_{pit}, where a strong potential dependence of the current emerges and stable pitting ensues.

Further inspection of Fig. 1a–h reveals that the anodic excursion span does not exhibit an active dissolution up to the potential corresponding to the appearance of the first meta-stable pitting events (current oscillations). The lack of active dissolution may be attributed to spontaneous passivation of Al. Passivity is due to the presence of an Al_2O_3 film on the electrode surface [16, 17]. These results demonstrate that the oxide film is stable in this range of potential. The passive oxide film formation may be explained on the basis that in deaerated neutral solutions, the main passivating (film forming) species are OH^- ions. These adsorb on the metal surface and promote repassivation following Eqs. 1 and 2

$$Al + OH^- = Al(OH)_{ads}^- \tag{1}$$

$$2Al(OH)_{ads}^- + H_2O = Al_2O_3 + 4H^+ + 6e^- \tag{2}$$

Figure 1i shows the passive region as a function of ClO_4^- concentration and %Si in the alloy. It is obvious that

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[1] In addition, after holding the electrode for 2 h at –0.40 V, potentiometric titration using chloride selective electrode (with a detection limit of 200 ppm) indicated that Cl^- ions, due to reduction of ClO_4^- ions, are not present in solution. This was the reason, as will be shown later, why we attributed passivity breakdown to the aggressive attack of ClO_4^- ion itself and not Cl^- ion.

the passive current density, j_{pass}, increases with increase in ClO_4^- concentration, and a slight increase in j_{pass} with applied potential is observed in all cases. These findings could be attributed to general weakness and thinning of the passive film as a result of adsorption of ClO_4^- ions on the oxide surface. This adsorption is expected to enhance as applied potential made more positive. The adsorbed ClO_4^- ions, as will be seen later, tend to enhance the dissolution of the oxide film. The decrease in j_{pass} with increase in Si content reflects the increased resistance of Al–Si alloys towards pitting attack.

There is significant amount of data in colloid and interface science indicating that ClO_4^- ions are bonding only electrostatically (weak adsorption) on the oxide surfaces, including aluminium oxide, hydrated aluminum oxide or passive aluminum, from aqueous media [18]. Despite the weak adsorption of ClO_4^- ions, there is some evidence from literature [19–21] and various studies in our lab [22–28] proving the occurrence of the pitting corrosion on the surface of some metals and alloys as a result of passivity breakdown by ClO_4^- ions. This means that the adsorption ClO_4^- ions, despite its weakness, has a significant role in passivity breakdown and initiation of pitting corrosion. This makes, without doubt, studying passivity breakdown of metals and alloys by aggressive ClO_4^- ions very interesting. However, owing to the weak adsorption of perchlorate ions, it is very important to declare here that the term "adsorption" of ClO_4^- ions always refers to "weak adsorption".

In the presence of ClO_4^- ions, there is a competition between OH^- ions (essential for passive film formation; Eqs. 1 and 2) and ClO_4^- ions (essential for passivity breakdown; Eqs. 3 and 4), for adsorption sites on the metal surface, consistent with Kruger's [29] adsorbed ion displacement model of passivity breakdown.

$$Al + ClO_4^- = Al(ClO_4)_{ads}^- \quad (3)$$

$$Al(ClO_4)_{ads}^- + nH_2O = Al(H_2O)_n^{3+} + ClO_4^- + 3e^- \quad (4)$$

If the rates of reactions 1 and 2 are faster than those of 3 and 4, film healing predominates. The converse causes local dissolution (pitting) to dominate. A soluble complex species, namely $A1(ClO_4)_{3(aq)}$ may then be formed according to Eq. 5:

$$Al(ClO_4)_{ads}^- + 2ClO_4^- = Al(ClO_4)_{3(aq)} + 3e^- \quad (5)$$

Generally, formation of a soluble complex species between aggressive anion and metal cation plays an important role in the pitting corrosion process [30]. The onset of passivity breakdown and initiation of pitting corrosion (E_{pit}) is now seen to arise as a simple consequence of the dissolution reactions (Eqs. 3 and 4) and subsequent formation of soluble complex species (Eq. 5) dominating over the film forming reactions (Eqs. 1 and 2) at the base of the flaw, resulting in pit formation. Galvele [31] demonstrated that electrochemical processes inside the pit are under mass-transfer control. The increased concentration of cations, due to metal dissolution, inside the pit leads to changes in localized solution chemistry. First, following Galvele [31], hydrolysis lowers the pH, as represented by the Eq. 6

$$Al(H_2O)_n^{3+} = Al(OH)_x^{(3-x)+} + (n-x)H_2O + xH^+ \quad (6)$$

A second effect arises from the well-recognized requirement that electrical neutrality must be maintained throughout the electrolyte. Therefore, aggressive ClO_4^- anions must migrate into the pit to compensate for the local increase in cation concentration, as shown by the theoretical analysis of Ateya and Pickering [32]. This leads to an increase in ClO_4^- concentration in the pit. The overall effect of the pit initiation process is to produce a micropit at the base of the flaw with a local solution chemistry that is enriched in ClO_4^- and H^+ species. This causes a greater imbalance between the film forming reactions and the dissolution reactions. Consequently, the pit once initiated, continues to propagate and enlarge.

It is worth noting from Fig. 1 that, within this perchlorate concentration range, oscillations in current form at potentials close to E_{pit}. The occurrence of these oscillations correspond to pits that only grow for a very short time and to a small depth. These pits have been called meta-stable pits [13, 33]. The occurrence of meta-stable pits in the passive region of Al is evidence that passivity, under these conditions, is not stable. When the meta-stable pits occur, the current first increases as pits nucleate and begin to grow, and then decreases after a short time [33]. Some pits however, become stable and continue to grow for longer periods of time to much greater depths [13, 33]. It is these stable pits that are important when considering the effects of corrosion damage. Stable pits and meta-stable pits are thought to be initiated in the same manner and stable pits are considered a subset of meta-stable pits [13]. Meta-stable pits unlike stable pits only grow to a very small size (~10 μm in diameter) at which stage their growth is arrested [14]. The only possible reason for these pits to cease growing in light of the reactivity of the metal is that the protective oxide coating is regenerated.

Similar to pure Al, Al–Si alloys exposed to aggressive perchlorate solutions exhibit meta-stable and stable pitting (inspect Fig. 1f–h), and therefore it is believed that they undergo the same stages of pit initiation, growth and then passivation or stable growth. The alloying constituents may have an effect upon the type, frequency and location of flaws within the oxide that result in meta-stable pits, but not on their occurrence [34]. The transition from meta-

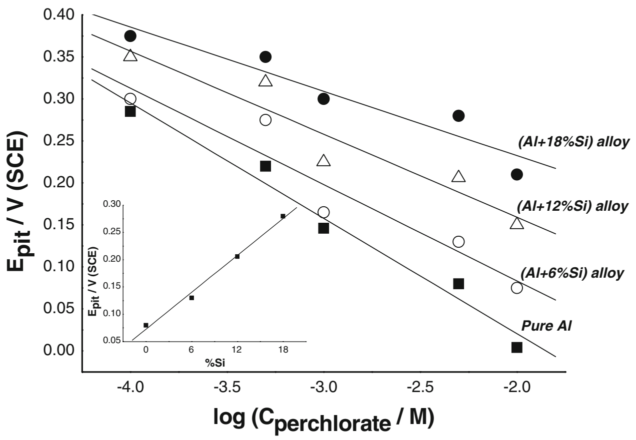

Fig. 2 Dependence of the pitting potential (E_{pit}) on log C$_{perchlorate}$ recorded for pure Al, (Al + 6%Si), (Al + 12%Si), and (Al + 18%Si) alloys at 25 °C

stable to stable pitting would be expected to occur in a similar manner to pure aluminium, by the acidification of the pit, even if a different pH is required to prevent passivation [34].

It is concluded that two types of pits exist, depending on perchlorate concentration and sample composition, those that are passivated and stop growing (metastable pits [13, 14, 33, 35]), and those that do not repassivate and continue to grow (stable pits). It can also be seen in the polarization curves presented in Fig. 1a–e that stable pit growth was more easily obtained, corresponding to a negative shift in E_{pit}, and the oscillations in current enhanced as the perchlorate concentration increased.

At a given perchlorate concentration (0.005 M), comparing Fig. 1f–h with Fig. 1d, it is obvious that these oscillations in current also depend on sample composition. Under these conditions, it is observed that oscillations in current decrease upon alloying Al with Si. The frequency of these oscillations decrease with an increase in %Si in Al (inspect Fig. 1f–h). In addition, both the pitting potential and the potential which coincides with the appearance of the first meta-stable pitting events are shifted in the noble direction. These results may indicate that the presence of Si, as an alloying element, in Al reduces the number and sizes of meta-stable pits. Consequently, this reduced the probability of generating stable pits. This, as will be shown below, may explain the positive shift observed in E_{pit} upon alloying Al with Si, corresponding to an increase in the pitting corrosion resistance of Al in these solutions.

Figure 2 represents the relationship between E_{pit}, recorded for Al and the three Al–Si alloys, and perchlorate concentration. Inspection of the data of Fig. 2 reveals that for all samples, an increase in ClO_4^- concentration shifts E_{pit} in the more negative (active) direction, corresponding to decreased resistance to pitting corrosion. It follows from the data of Fig. 2 that at a given ClO_4^- concentration, the values of E_{pit} decrease in the order: (Al + 18%Si) > (Al + 12%Si) > (Al + 6%Si) > Al, indicating that the pitting corrosion resistance of the four samples decreases in the same sequence. It seems that the presence of Si, as an alloying element, increases the pitting corrosion resistance of Al in aggressive perchlorate solutions. This increase in the pitting corrosion resistance of (Al–Si) alloys enhances with increasing Si content in the alloy. This is clearly seen from the positive shift observed in the values of E_{pit} with an increase in %Si in Al samples, as shown in the insert of Fig. 2.

The role played by Si in enhancing the pitting corrosion resistance of Al in these solutions may be explained on the basis that any localized dissolution will preferentially dissolve Al and leave the surface enriched in unreactive Si atoms. Enrichment of alloy surface in unreactive Si atoms during dissolution blocks the active sites available for Al dissolution. At this stage, dissolution is retarded and pitting ceases. In order for pitting to recommence, the potential must be raised even higher [to $(E_{pit})_{alloy}$] to activate dissolution at the less favourable sites. As the Si content is increased, Si atoms will appear with greater frequency. Therefore, dissolution processes will be retarded until increasingly higher potentials are reached. Therefore, $(E_{pit})_{alloy}$ must increase with Si content, as shown in the insert of Fig. 2. Other research workers attributed the high corrosion resistance of Al-Si alloys to the incorporation of Si atoms in the Al_2O_3 passive film [36]. This incorporation repairs the film defects and precludes significant dissolution of the oxide film [37]. This makes it more difficult for ClO_4^- ions to migrate through the oxide film. Si would as a result increase the difficulty of soluble film formation required for film rupture to occur [30]. Si may also slow down the rate of metal dissolution by reducing the amount of free metal ions in the pit solution resulting in a decrease in diffusion of ClO_4^- into the pit and reduction in diffusion of metal cations out of the pit [38]. It also probable that the presence of Si in Al assists the rapid repassivation of the bare metal so that further metal dissolution and, therefore, meta-stable pit formation is prevented.

3.1.2 *Effect of inorganic inhibitors*

The polarization responses of Al have been studied in 0.005 M $NaClO_4$ solution in the absence and presence of various concentrations of K_2CrO_4, Na_2SiO_3, Na_2MoO_4 and Na_2WO_4 as inorganic inhibitors. Figure 3a–d represents polarizations carried out on Al in 0.005 M $NaClO_4$ solution and separately in 0.005 M $NaClO_4$ solution containing 0.001 M of the inhibitor at a scan rate of 1.0 mV s^{-1} starting from −0.40 V (SCE) until stable pitting occurred. In all cases, the polarization curves show a passive region,

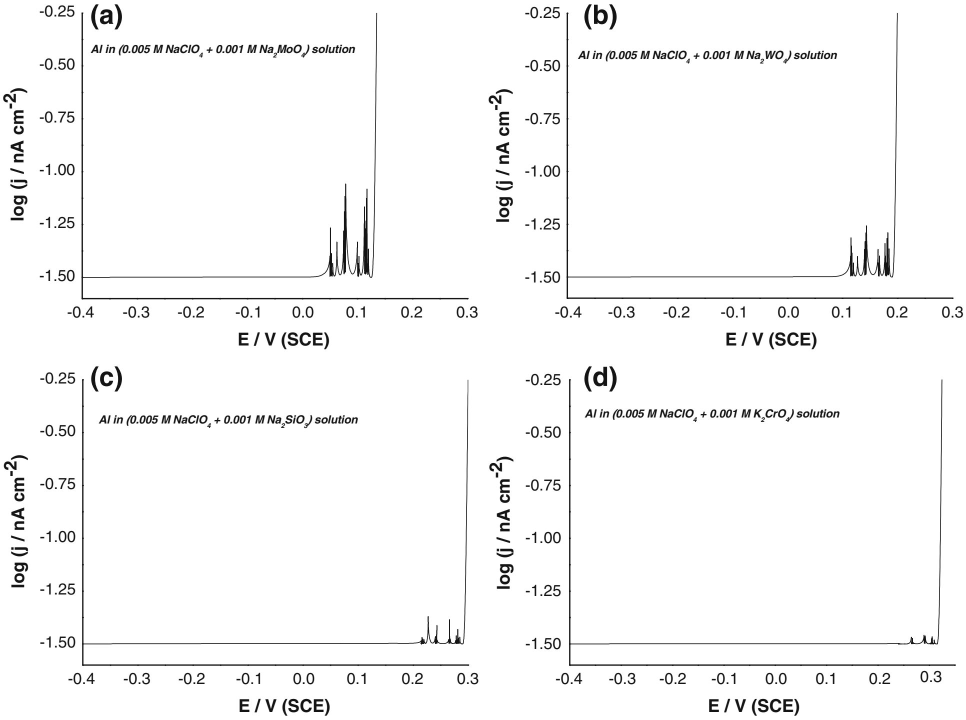

Fig. 3 Potentiodynamic anodic polarization curves recorded for pure Al in 0.005 M $NaClO_4$ solution containing 0.001 M of Na_2SiO_3, K_2CrO_4, Na_2WO_4 and Na_2MoO_4 (as inorganic inhibitors) at a scan rate of 1.0 mV s^{-1} and at 25 °C

meta-stable pitting (indicated by current oscillations) and a pitting potential, E_{pit}, (indicated by a permanent rise in current in the passive region). It is obvious that both the pitting potential and the potential which coincides with the appearance of the first meta-stable pitting events are shifted in the noble direction in the presence of these inhibitors. An extension of the passive region results, corresponding to a retardation in the meta-stable and stable pitting events. It is observed that E_{pit} is increased by 50, 115, 320 and 340 mV in the presence of WO_4^{2-}, MoO_4^{2-}, SiO_3^{2-} and CrO_4^{2-}, respectively. These values indicate that SiO_3^{2-} and CrO_4^{2-} were better inhibitors than MoO_4^{2-} and WO_4^{2-} under these experimental conditions. It has been shown that the meta-stable pitting determines the susceptibility of metals and alloys to stable pitting [39]. Since the principle reason for adding inhibitors to aggressive solutions is to inhibit stable pitting, it is expected that the inhibition of stable pitting would involve the retardation of the meta-stable pitting events on the metal. Results of the present work showed that silicate and chromate retard effectively the occurrence and growth of meta-stable pitting events, and consequently affects stable pitting (inspect Fig. 3c, d).

Figure 4 depicts the relationship between the pitting potential (E_{pit}) and the logarithmic concentration of the inhibitors [log ($C_{inhib.}$/M)] recorded for pure Al in 0.005 M $NaClO_4$ solution devoid of and containing various concentrations of the four tested inorganic inhibitors. In all cases it is observed that the pitting potential increases with increase in inhibitors' concentration. These results indicate that stable pitting events, and therefore the rate of stable pit growth, retarded in presence of these inhibitors. In addition at a fixed inhibitor's concentration, the pitting potential was found to increase in the order: $MoO_4^{2-} < WO_4^{2-} << SiO_3^{2-} \approx CrO_4^{2-}$. These results confirm the findings that SiO_3^{2-} and CrO_4^{2-} inhibit meta-stable and stable events more effectively than MoO_4^{2-} and WO_4^{2-}.

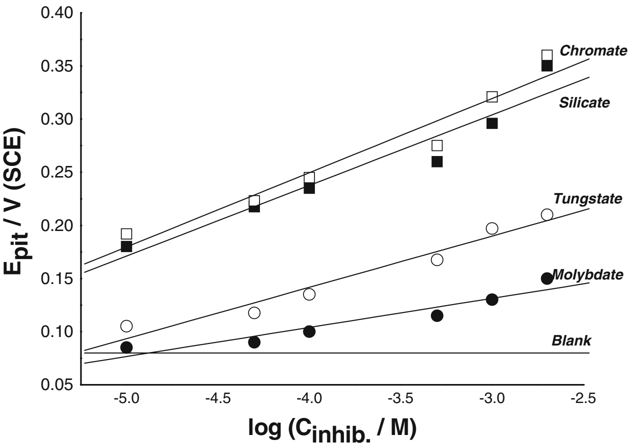

Fig. 4 Dependence of the pitting potential (E_{pit}) on log $C_{inhib.}$ recorded for pure Al in 0.005 M $NaClO_4$ solution in the absence and presence of various concentrations of Na_2SiO_3, K_2CrO_4, Na_2WO_4 and Na_2MoO_4 (as inorganic inhibitors) at 25 °C

Further, the effect of these four inhibitors on the incubation time (t_i) of pitting corrosion was studied (Fig. 5). The samples were first passivated at −600 mV (SCE) in 1.0 M Na_2SO_4 solution for 15 min, in order to get a stable

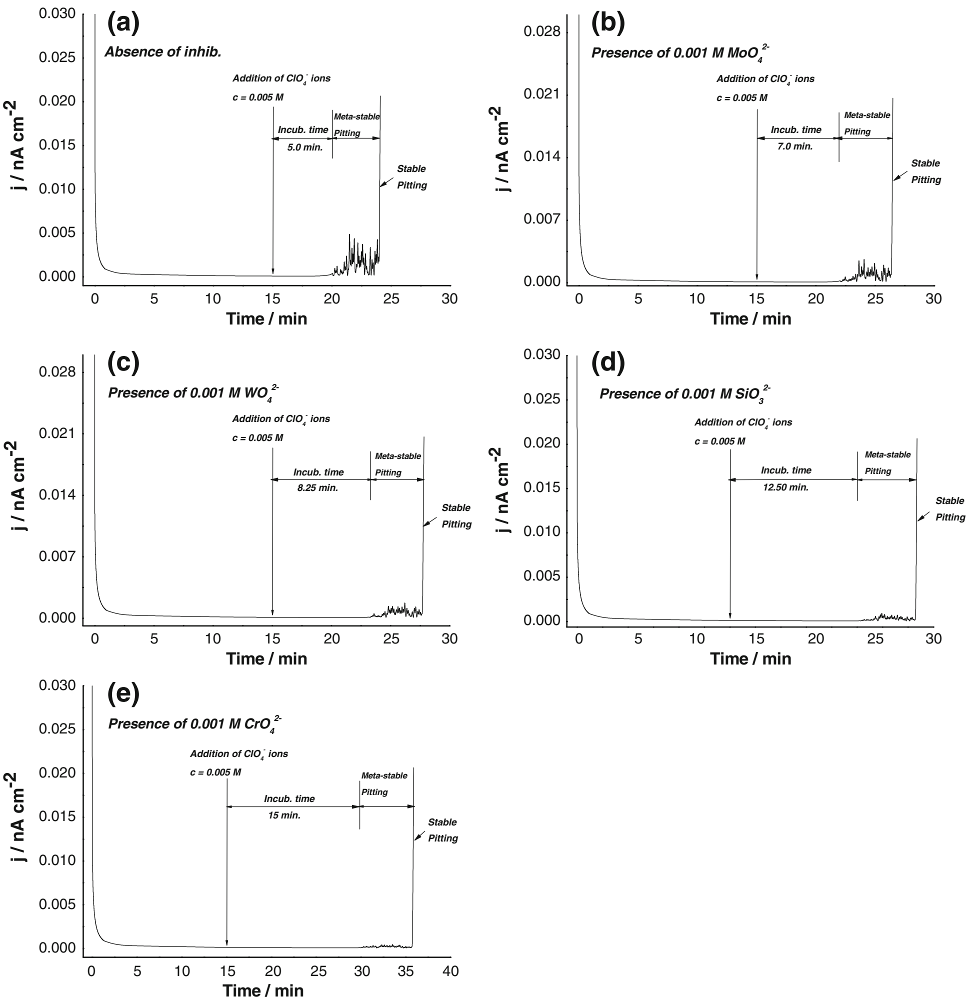

Fig. 5 Potentiostatic current/time transients recorded for pure Al in 1.0 M Na_2SO_4 solution at 25 °C and at a step anodic potential ($E_{s,a}$) of −600 mV (SCE), followed by addition (after 15.0 min) of $NaClO_4$ (0.005 M) without and with 0.001 M of the four tested inorganic inhibitors

Al_2O_3 film on the electrode surface [28], and then $NaClO_4$ was added to the sulphate solution to establish a 0.005 M perchlorate concentration. Exactly the same procedure was followed for Al in 1.0 M Na_2SO_4 solution containing 0.005 M $NaClO_4$ + 0.001 M of the inhibitor. Within this study the incubation time was defined as the time period form perchlorate addition until significant current transient activity could be detected-indicating the occurrence of meta-stable pitting (Fig. 5). This definition was chosen since the onset of meta-stable pitting is much more associated with the very early initiation stages of pitting corrosion than the incubation time for stable pit growth, which is often affected and controlled by a number of factors [38, 40].

Upon the addition of aggressive ClO_4^- ions to sulphate solution, a significant degree of meta-stable pitting, reflected by the frequent fluctuations in the current in Fig. 5a, was observed. However, this current noise tends to decrease upon the addition of WO_4^{2-} and MoO_4^{2-} (Fig. 5b, c) and removed almost completely in the presence of SiO_3^{2-} and CrO_4^{2-} (Fig. 5d, e), indicating the absence of meta-stable pitting attack. In addition, an increase in the incubation time (t_i) was observed. The incubation time is increased by 7.0, 8.25, 12.5 and 15.0 min in the presence of WO_4^{2-}, MoO_4^{2-}, $SiO_3^{2-}$and CrO_4^{2-}, respectively. This is consistent with the finding that $SiO_3^{2-}$and CrO_4^{2-} were better inhibitors than WO_4^{2-} and MoO_4^{2-}. It seems that meta-stable pits find it more difficult to develop in the presence of the inhibitors. The transition from meta-stable to stable pitting has therefore been made more difficult by the inhibitors.

These findings can be confirmed by plotting the relation between the rate of meta-stable pitting initiation, defined as t_i^{-1}, for pure Al and log $C_{inhib.}$ (Fig. 6). It follows from the data of Fig. 6 that for all inhibitors the rate of initiation of meta-stable pitting events decreases with increasing their concentrations. The decrease of the rate of meta-stable pitting initiation with inhibitors' concentration may be explained on the basis that the inhibitors block the active sites available for a meta-stable pit initiation. These results support the findings that meta-stable pits find it more difficult to develop in the presence of the inhibitors. At a

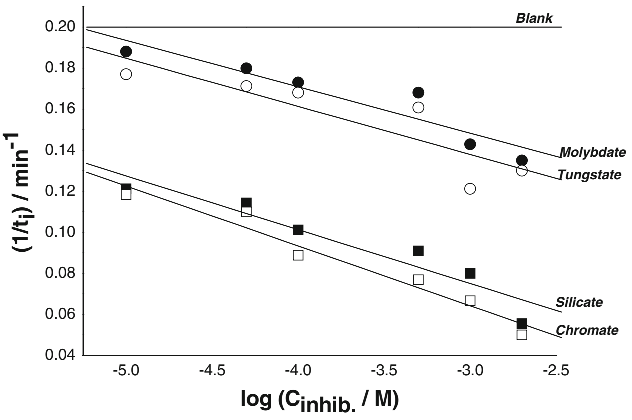

Fig. 6 Dependence of the rate of meta-stable pit growth (t_i^{-1}) on log C$_{inhib.}$ recorded for pure Al in 0.005 M $NaClO_4$ solution in the absence and presence of various concentrations of Na_2SiO_3, K_2CrO_4, Na_2WO_4 and Na_2MoO_4 (as inorganic inhibitors) at 25 °C

Table 1 The radii and volumes (assuming perfect spheres) of ClO_4^-, SiO_3^{2-}, CrO_4^{2-}, WO_4^{2-} and MoO_4^{2-} [49]

Anion	ClO_4^-	SiO_3^{2-}	CrO_4^{2-}	WO_4^{2-}	MoO_4^{2-}
Radius (nm)	0.225	0.195	0.229	0.237	0.231
Volume (nm^3)	0.0477	0.0310	0.0503	0.0557	0.0516

given inhibitors' concentration (0.001 M), the rate of meta-stable pit initiation decreases in the sequence: $MoO_4^{2-} < WO_4^{2-} << SiO_3^{2-} \approx CrO_4^{2-}$. These results confirm the greater effectiveness of SiO_3^{2-} and CrO_4^{2-} in retarding meta-stable events compared with MoO_4^{2-} and WO_4^{2-}.

Under the field assisted migration mechanism [39], the inhibitor species penetrate the oxide film in parallel with ClO_4^- ions under the influence of the electric field. Penetration of aggressive (and inhibiting) ions is thus expected to occur preferentially at active sites. The inhibitors would have either to hinder or to prevent completely the migration of aggressive ClO_4^- ions through the oxide film. This could be achieved by improving the oxide film. These inhibitors may improve the oxide film by incorporation into the defective film sites, and subsequent reduction into stable oxides, following Eqs. 7–9:

$$2CrO_4^{2-} + 6e^- + 5H_2O = Cr_2O_3 + 10OH^- \quad (7)$$

$$WO_4^{2-} + 2e^- + 2H_2O = WO_2 + 4OH^- \quad (8)$$

$$MoO_4^{2-} + 2e^- + 2H_2O = MoO_2 + 4OH^- \quad (9)$$

The reduced forms of the inhibitors, namely Cr_2O_3, WO_2 and MoO_2 may be incorporated in the passive film and tend to repair any flawed regions on the surface. This may either change the electronic properties for instance by reversing the ion selectivity [41–43] of the film making it more difficult for ClO_4^- ions to migrate through it, or take part in enhancing the oxide film by increasing its thickness [44]. The possibility of any of these occurring is still being debated. These inhibitors as a result increase the difficulty of soluble film formation required for film rupture to occur [30]. This difficulty in soluble film formation prevents direct contact of the bare metal surface with aggressive ClO_4^- ions so that further metal dissolution and, therefore, meta-stable pit formation is prevented.

A further explanation for the inhibiting ability of K_2CrO_4, Na_2MoO_4 and Na_2WO_4, as indicated by Eqs. 7–9, is that they reduce the local acidity at the sites where they react. Equation 7, as an example, shows that for 2 mol of CrO_4^{2-} reduced, 5 mol of H_2O are consumed and 10 mol of OH^- ions are produced which increase local pH. This would affect the transition from meta-stable to stable pitting since a low pH is important to maintain the aggressiveness necessary for pit development.

The mechanism of pitting corrosion inhibition of Al in ClO_4^- solutions by silicates can be explained adopting the work of Aramaki [45]. In a part of his study, he examined inhibition of Zn pitting corrosion in 0.50 M NaCl solution by sodium silicate using X-ray photoelectron spectra (XPS). The XPS spectra indicated that the Zn surface was covered with a layer composed of zinc hydroxide and a small amount of silicate with no chloride ions being detected. He concluded that zinc silicate precipitates at defects within this surface layer preferentially, to prevent pitting corrosion. This was elucidated by electron probe microanalysis (EPMA) [46].

Another factor, which might affect the strength of an inhibitor, is the size of the inhibiting species. It is important to determine whether the inhibitor species are able to penetrate or be pulled through the oxide film under the influence of the electric field. Table 1 shows the radii and volumes (assuming perfect spheres) of ClO_4^- and polyatomic anions of the inhibitors [47]. These radii are comparable. It is therefore possible for these polyanions to be pulled through the oxide film under the influence of an electric field since they are not much larger than the ClO_4^- ion. Once these inhibitor species migrate through the oxide film, they reduce the amount of ClO_4^- ions, which eventually migrate to a particular site to react and cause a rupture. This might increase the proportion of small meta-stable pits, corresponding to low current noise, as observed in Fig. 5d, e, since the large amounts of ClO_4^- ions required for the formation of soluble species to activate pitting would not be readily accumulated.

Because these ions carry a negative charge as ClO_4^- it also suggests that ClO_4^- ions would be repelled from these sites. Thus the rate at which ClO_4^- ions migrate through the oxide film will be reduced by the parallel migration of other species. This would cause a reduction in the probability of generating meta-stable pits, and therefore the rate of stable pit growth ceases. It is also possible that the presence of these inhibitor species assists in repairing defects (may be via repassivation) of the oxide film so that further metal dissolution and, therefore, meta-stable pit formation is prevented. Repassivation may be enhanced because the amount of ClO_4^- ions present at these sites in the presence of the inhibitors is reduced. This would also make the transition from meta-stable to stable pit growth more difficult because the necessary amount of ClO_4^- ions required for transition to take place is no longer available.

The probability of generating stable pits is largely controlled by the ability to generate meta-stable pits capable of attaining the "critical pit stability product" [13, 48, 49]. A general reduction in the number of meta-stable pits reduces the possibility of developing such damaging meta-stable pits. The only way for an inhibitor to be effective during the meta-stable pitting stage is by reducing the rate of anodic dissolution (in the meta-stable pits) so that the attainment of the critical pit stability product is prevented [13, 39, 49]. This makes the possibility of generating meta-stable pits, which are capable of attaining the critical pit stability product, and hence stable pits more difficult. Despite the marked reductions in the occurrence of meta-stable pits by the presence of the inhibitors, stable pitting still occurs. This signifies that not all the sites on the metals are prevented from generating stable pits [50].

4 Conclusion

The effect of alloyed Si and some inorganic inhibitors on the meta-stable and stable pitting events on the surface of pure Al and three Al–Si alloys have been studied in deaerated neutral $NaClO_4$ solutions of various concentrations (10^{-4}–10^{-2} M) using potentiodynamic anodic polarization and potentiostatic techniques. The meta-stable pitting events occurring on Al and the three Al–Si alloys were able to give useful information about their susceptibility to pitting corrosion. Once the meta-stable pits propagate, they grow resulting in an increase in the probability of generating stable pits. The presence of Si, as an alloying element in Al, and inorganic inhibitors (Na_2SiO_3, K_2CrO_4, Na_2WO_4 and Na_2MoO_4) in aggressive perchlorate solutions reduces the rate of formation of meta-stable pits, corresponding to a reduction in the probability of developing stable pits, and an increase in the pitting potential results. This makes attainment of stable pit growth more difficult. Na_2SiO_3 and K_2CrO_4 were found to be more effective than Na_2WO_4 and Na_2MoO_4 in inhibiting meta-stable and stable pitting events.

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