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Morphological studies of the mechanism of pit growth of pure aluminum in sulfate ion- or nitrate ion-containing 0.1 M NaCl solutions

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Abstract The mechanism of pit growth of pure aluminum (Al) in sulfate ion (SO_4^{2-})- or nitrate ion (NO_3^-)-containing 0.1 M sodium chloride solutions has been studied in terms of the morphological changes of artificial pits using potentiodynamic polarization experiment, potentiostatic current transient technique and optical microscopy. The increase in SO_4^{2-} and NO_3^- ion concentrations in NaCl solution raised the pitting potential E_{pit} of pure Al, which is ascribed to the impediment to pit initiation on pure Al by the addition of SO_4^{2-} or NO_3^- ions. From the potentiostatic current transients of artificial pits in aqueous 0.1 M NaCl solution, the average value of the pit current was observed to increase with increasing SO_4^{2-} ion concentration, whereas that value of the pit current in the presence of NO_3^- ions increased up to ca. 0.4 M NO_3^- ion concentration and then decreased abruptly with increasing NO_3^- ion concentration. From observations of the morphologies of the pits, it appears that the pit grows preferentially in the lateral direction or in the downward direction by adding SO_4^{2-} or NO_3^- ions to aqueous 0.1 M NaCl solution, respectively. Based upon the experimental results, two different pit growth mechanisms by anion additives can be proposed: (1) pit growth by the preferential attack of both SO_4^{2-} and Cl^- to the pit wall in SO_4^{2-} -containing solutions; (2) pit growth by the creation of an aggressive environment at the pit bottom up to 0.4 M NO_3^- ion concentration due to the lower mobility of NO_3^- than Cl^- in NO_3^- -containing solutions.

Keywords Aluminum · Sulfate ion · Nitrate ion · Artificial pit · Pit growth

Introduction

Generally, it is recognized that pitting corrosion of pure aluminum (Al) occurs in solutions containing halide ions (F^- , Cl^- , Br^- , I^-) [1, 2, 3]. Thus, the anion composition of the solution has a great influence on the pitting corrosion of Al. In this respect, the inhibition effects of various anion additives on the pitting corrosion of pure Al have been widely investigated in aqueous chloride solutions [4, 5, 6, 7, 8, 9, 10] and, as a result, competitive adsorption of the anion has been regarded as a primary inhibition mechanism of pitting corrosion of pure Al by many researchers [4, 6, 7, 8, 9, 10].

Among various inhibitive anions, it is well known that SO_4^{2-} and NO_3^- ions retard the pitting corrosion of pure Al in chloride solutions [4]. Recently, Pyun and Moon [10] suggested that pitting corrosion of pure Al in SO_4^{2-} - or NO_3^- -containing chloride solutions can be impeded by the competitive adsorption of SO_4^{2-} ions and by the incorporation of NO_3^- ions, respectively.

Pitting corrosion is characterized by two stages of pit initiation and growth. Until now, however, the overwhelming majority of investigations on pitting corrosion of Al have been related only to pit initiation and less attention has been paid to the mechanism concerning the effect of anion additives on pit growth.

Because the morphology of corrosion pits represents a time-averaged record of the anodic processes which control the rate of corrosion [11, 12], the change in the morphology of the pits with the environmental conditions has been widely studied during propagation [11, 12, 13, 14, 15, 16, 17]. In previous work [17], the effect of bicarbonate (HCO_3^-) ions on the pitting corrosion of 316L stainless steel was investigated in terms of the morphological changes of pits with HCO_3^- ion concentration. However, in that work, since the morphology of the pits changed during pit initiation and pit growth, the

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role of the HCO_3^- ion in the morphology of a growing pit in chloride solutions has not been clearly examined.

In the present work, the effects of SO_4^{2-} and NO_3^- ion additives on pit growth of pure Al have been investigated in 0.1 M NaCl solution as a function of anion concentration using potentiodynamic polarization experiment, potentiostatic current transient technique and optical microscopy. For this purpose, we made an artificial pit in pure Al to simulate the condition of pure pit growth experimentally. On the basis of the experimental results, two different mechanisms for pit growth in pure Al by SO_4^{2-} and NO_3^- ion additives have been proposed.

Experimental

The specimen used in this investigation was a 99.999% purity Al rod (Aldrich) of 6.35 mm diameter. The rod electrodes were set in a block of polyethylene and the upper surface of the block was ground with silicon carbide papers to 1200 grit to expose the cross section of the electrodes to the solution. The electrolytes used in this study were 0.1 M NaCl solutions containing various Na_2SO_4 or NaNO_3 concentrations (0, 0.1, 0.2, 0.3, 0.4 and 0.5 M). In all the electrochemical experiments the electrolyte was exposed to the air and stagnant. A platinum mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

In order to elucidate the effects of SO_4^{2-} and NO_3^- ion additives on the pit growth of pure Al, an artificial pit was made on the Al surface by drilling hole of 1 mm diameter and 1 mm depth. The surface of the Al specimens with the artificial pit was coated with a fast drying lacquer with the exception of the artificial pit.

Potentiodynamic polarization measurements were conducted on the pure Al rod specimen with a scan rate of 0.5 mV s^{-1} in the applied potential range from -1.2 to $+2.2 \text{ V}_{\text{SCE}}$ by using an EG&G model 263A galvanostat/potentiostat. The pitting potential (E_{pit}) of pure Al in the absence of SO_4^{2-} and NO_3^- ions was compared with those in their presence.

The current of the artificial pit was recorded with time potentiostatically at an applied anodic potential of $+0.8 \text{ V}_{\text{SCE}}$ to examine the effects of SO_4^{2-} and NO_3^- ion additives on the growth of artificial pits in the Al specimens. In order to experimentally simulate the conditions of the pure pit growth process, the artificial pit on the specimen was firstly subjected to a constant anodic potential of $+0.8 \text{ V}_{\text{SCE}}$ in 0.1 M NaCl solution for 2 h before adding the anions. After that, the change in the current was recorded with time for 6 h during the growth of artificial pits in SO_4^{2-} - or NO_3^- -containing NaCl solution.

After the potentiostatic current transient experiments, cross-sectional views of the artificial pits were observed by optical microscopy to detect morphological changes of the grown pit with various SO_4^{2-} and NO_3^- ion concentrations. All the experiments were conducted at 25°C .

Results and discussion

Retardation of pit initiation by SO_4^{2-} and NO_3^- ions

Figures 1 and 2 show potentiodynamic polarization curves obtained from a pure Al rod specimen at a scan rate of 0.5 mV s^{-1} in aqueous 0.1 M NaCl solutions containing various SO_4^{2-} or NO_3^- ion concentrations (0, 0.1, 0.2, 0.3, 0.4 and 0.5 M). As the concentrations of SO_4^{2-} or NO_3^- increased, E_{pit} shifted to more positive values, indicating the impediment to pit initiation of

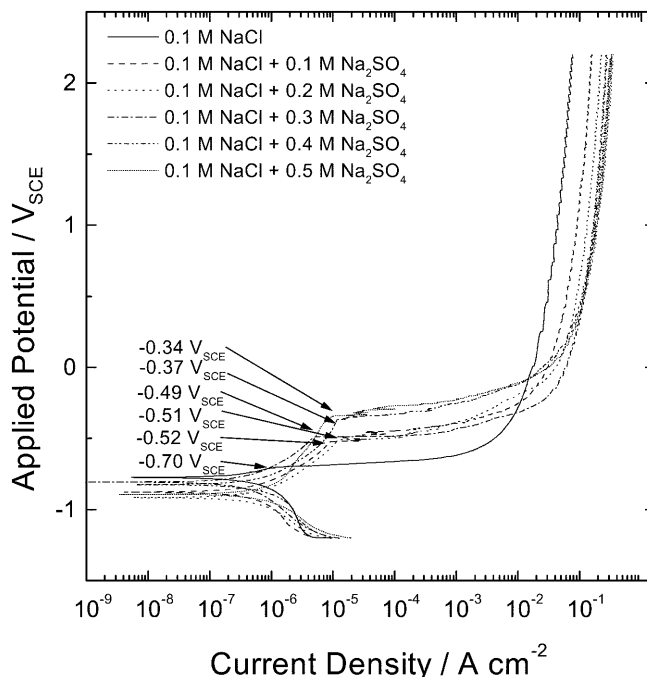


Fig. 1 Potentiodynamic polarization curves of pure Al with a scan rate of 0.5 mV s^{-1} in aqueous 0.1 M NaCl solutions containing various SO_4^{2-} ion concentrations

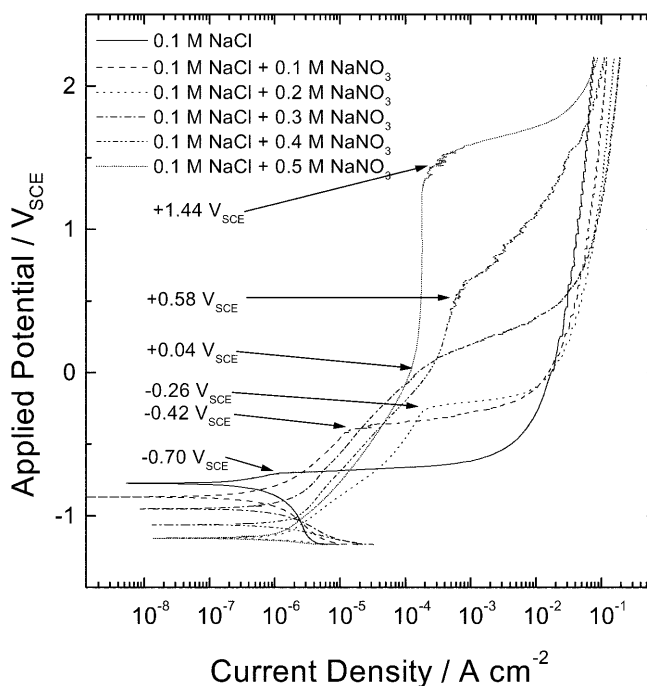


Fig. 2 Potentiodynamic polarization curves of pure Al with a scan rate of 0.5 mV s^{-1} in aqueous 0.1 M NaCl solutions containing various NO_3^- ion concentrations

pure Al by the addition of SO_4^{2-} or NO_3^- ions. This is caused by the competitive adsorption of SO_4^{2-} ions with Cl^- ions and by the incorporation of NO_3^- ions into the oxide film, respectively [10].

Mechanism of pit growth by SO_4^{2-} ion additives

In Fig. 1 it is worthwhile to note that at potentials above E_{pit} the current density reached a steady-state value, resulting from the precipitation of a salt film onto the Al surface [18, 19]. Simultaneously, the value of the steady-state current density increased with increasing concentrations of SO_4^{2-} ions in 0.1 M NaCl solution, due mainly to the increase in solution conductivity [20]. This implies that SO_4^{2-} ions accelerate the pit growth of pure Al in NaCl solution.

For comparison of the morphological changes of artificial pits in SO_4^{2-} - or NO_3^- -free 0.1 M NaCl solution with those in SO_4^{2-} - or NO_3^- -containing 0.1 M NaCl solutions, potentiostatic current transient experiments were performed in 0.1 M NaCl solution. The cross-sectional view of the artificial pit grown at a constant potential of $+0.8 V_{\text{SCE}}$ in 0.1 M NaCl solution at growing time of 6 h is shown in Fig. 3. It is noted that the inside of the pit was uniformly dissolved by Cl^- ion attack.

Figure 4 gives the value of the average pit current obtained from the potentiostatic current transients for the artificial pits of pure Al as a function of SO_4^{2-} ion concentration in aqueous 0.1 M NaCl solution. The value of the average pit current is defined by $i = \Delta Q / \Delta t$, where ΔQ is the amount of charge that passes over time Δt . The value ΔQ was calculated from the potentiostatic current transients by integrating the pit current with respect to time. It was found that the value of the average pit current rose as the concentration of the SO_4^{2-} ions increased. This implies that the artificial pit grows more rapidly in SO_4^{2-} -containing NaCl solution than in SO_4^{2-} -free NaCl solution.

Figure 5 presents the changes in the cross-sectional views of the artificial pits of pure Al subjected to a constant anodic potential of $+0.8 V_{\text{SCE}}$ for 6 h in 0.1 M NaCl solution containing various SO_4^{2-} ion concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M). In the figure it is readily seen that the width of the artificial pit in the presence of SO_4^{2-} ions is noticeably larger compared to

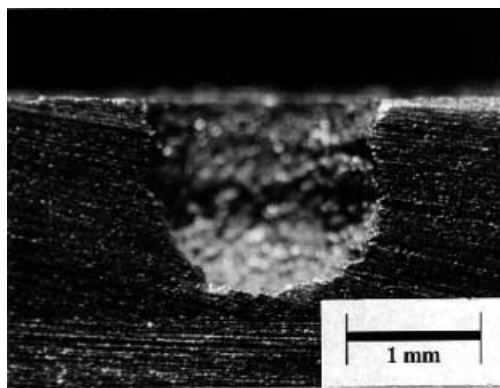


Fig. 3 Cross-sectional view of a grown artificial pit of pure Al subjected to a constant anodic potential of $+0.8 V_{\text{SCE}}$ in aqueous 0.1 M NaCl solution for 6 h

that in their absence (see Fig. 3) and the depth of the pit in the presence of SO_4^{2-} ions is shortened compared to that in their absence (see Fig. 3). This was attributed to a higher dissolution rate at the pit wall in SO_4^{2-} -containing NaCl solutions compared with that in SO_4^{2-} -free solutions, and the retardation of active dissolution at the pit bottom due to the precipitation of $\text{Al}_2(\text{SO}_4)_3$ in SO_4^{2-} -containing NaCl solutions.

It was reported that addition of SO_4^{2-} ions to NaCl solutions enhances the anodic dissolution after film breakdown [21, 22]. Thus, the pit wall is more actively dissolved owing to the attack of both SO_4^{2-} and Cl^- . Since the mobility of SO_4^{2-} is higher than that of Cl^- [23], as shown in Table 1, the concentration ratio of SO_4^{2-} to Cl^- in the solution will increase as a function of depth into the pit. The mass transport of Al^{3+} ions occurs slowly from the pit bottom through the pit solution to the solution bulk and hence Al^{3+} ions are supersaturated in the forms of $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 at the pit bottom. Considering that the solubility of $\text{Al}_2(\text{SO}_4)_3$ is lower than that of AlCl_3 in water [24] (Table 2), it is conceivable that the precipitation of $\text{Al}_2(\text{SO}_4)_3$ dominates. It is thus suggested that the formation of $\text{Al}_2(\text{SO}_4)_3$ retards the active dissolution of Al at the pit bottom.

Mechanism of pit growth by NO_3^- ion additives

Figure 6 demonstrates the change in the value of the average pit current as a function of NO_3^- ion concentration in 0.1 M NaCl solution. It was found that the value of the average pit current increased up to NO_3^- ion

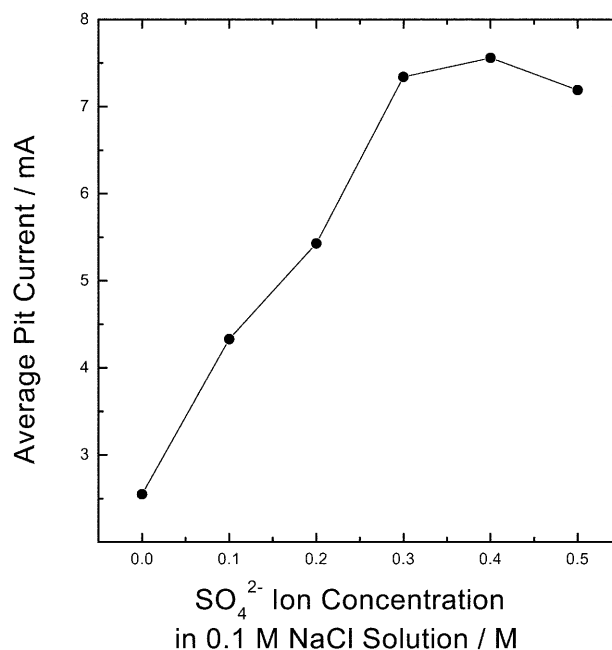


Fig. 4 Changes in the values of the average pit current with various SO_4^{2-} ion concentrations in 0.1 M NaCl solution during artificial pit growth

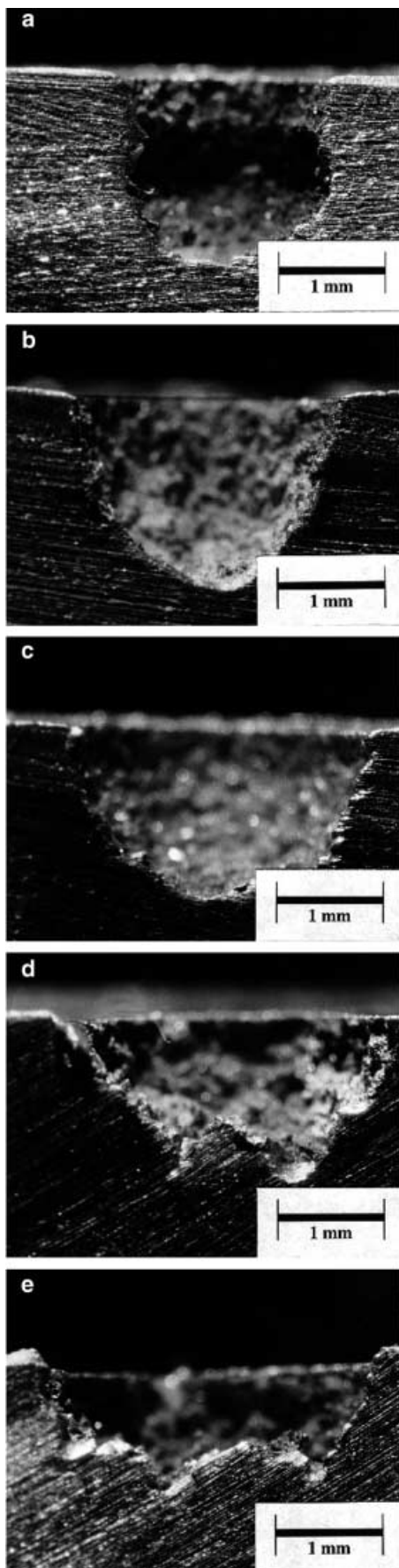


Fig. 5 Cross-sectional views of the grown artificial pits of pure Al subjected to a constant anodic potential of $+0.8 V_{SCE}$ for 6 h in aqueous 0.1 M NaCl solution containing various SO_4^{2-} concentrations: **a** 0.1 M, **b** 0.2 M, **c** 0.3 M, **d** 0.4 M, **e** 0.5 M

Table 1 The mobilities of Cl^- , SO_4^{2-} and NO_3^- ions in water at 25 °C

| Ion | Mobility ($cm^2 s^{-1} V^{-1}$) |
|-------------|-----------------------------------|
| Cl^- | 7.9×10^{-4} |
| SO_4^{2-} | 8.3×10^{-4} |
| NO_3^- | 7.4×10^{-4} |

Table 2 The solubilities of $AlCl_3$, $Al_2(SO_4)_3$ and $Al(NO_3)_3$ in water at 25 °C

| Aluminum salt | Solubility (g/100 g water) |
|----------------|----------------------------|
| $AlCl_3$ | 31.1 |
| $Al_2(SO_4)_3$ | 27.82 |
| $Al(NO_3)_3$ | 43.5 |

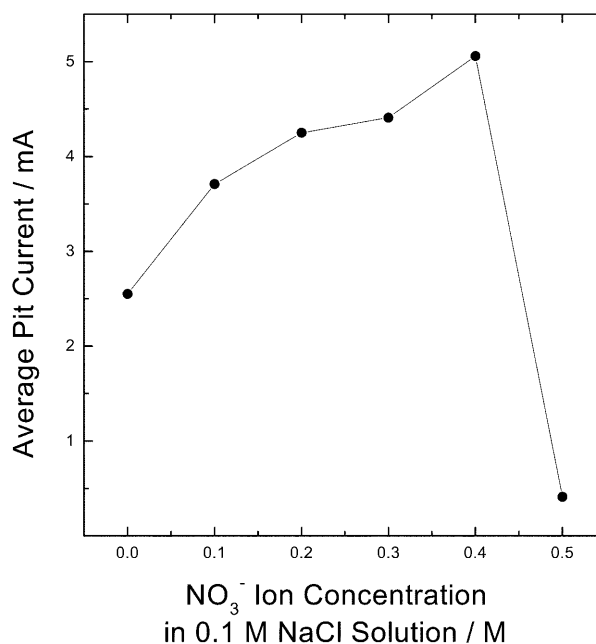


Fig. 6 Changes in the values of the average pit current with various NO_3^- ion concentrations in 0.1 M NaCl solution during artificial pit growth

concentrations around 0.4 M and then decreased abruptly with increasing NO_3^- ion concentration.

Figure 7 illustrates the change in the cross-sectional views of the artificial pits of pure Al subjected to a constant anodic potential of $+0.8 V_{SCE}$ for 6 h in 0.1 M NaCl solution containing various NO_3^- ion concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 M). In Fig. 7a–d it is shown that the pits grow deeper in the presence of NO_3^- ions. This is the result of enhanced Al dissolution at the

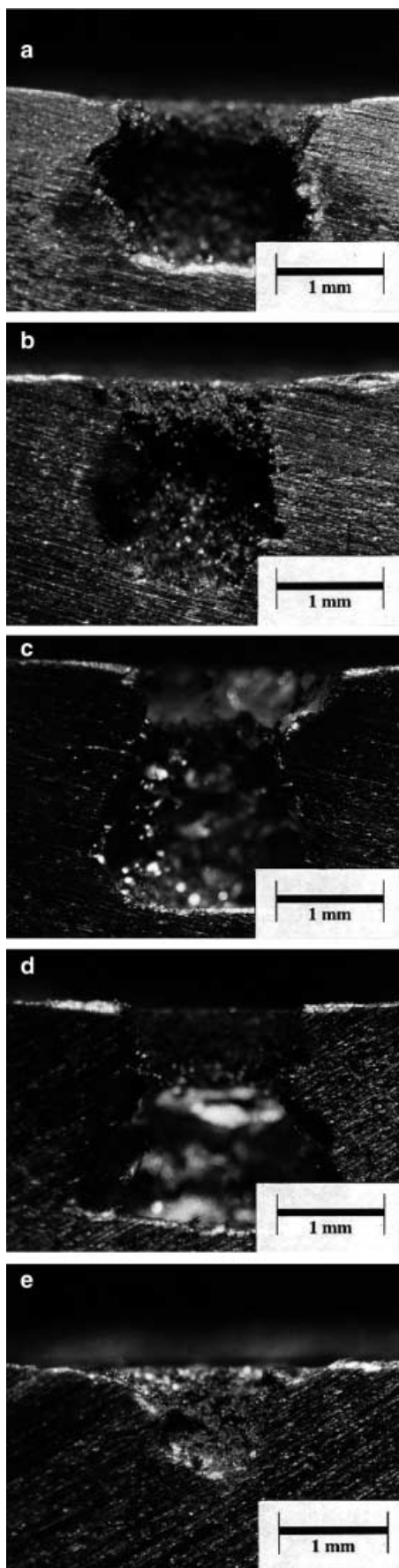


Fig. 7 Cross-sectional views of the grown artificial pits of pure Al subjected to a constant anodic potential of $+0.8 V_{SCE}$ for 6 h in aqueous 0.1 M NaCl solution containing various NO_3^- concentrations: **a** 0.1 M, **b** 0.2 M, **c** 0.3 M, **d** 0.4 M, **e** 0.5 M

pit bottom. However, in 0.1 M NaCl+0.5 M NaNO₃ solution the growth of the pit is suppressed, as can be seen in Fig. 7e.

Since the mobility of Cl^- is higher than that of NO_3^- , the concentration ratio of NO_3^- to Cl^- will decrease as a function of depth into the pit. The decrease in the concentration ratio of NO_3^- to Cl^- with pit depth results in the transition from passivation at the pit wall to active dissolution at the pit bottom. Therefore, attack of Cl^- at the pit bottom dominates over that at the pit wall, which leads to an enhanced dissolution in the downward direction. In addition, considering that the solubility of $Al(NO_3)_3$ is higher than that of $AlCl_3$ in water, the formation of $Al(NO_3)_3$ will contribute to a faster dissolution of Al at the pit bottom. As the pit elongates, the environment at the pit bottom will become more occluded. A lower pH and more aggressive chemistry may result, causing a higher dissolution rate. Above a NO_3^- ion concentration of 0.4 M, since the value of the NO_3^- ion concentration in the solution bulk is very high, it is plausible that the concentration ratio of NO_3^- to Cl^- at the pit bottom is high enough to passivate the pit bottom, resulting in the retardation of artificial pit growth, as shown in Fig. 7e.

From Figs. 5 and 7, the value of the aspect ratio of the pit was calculated as a function of anion additive concentration. The aspect ratio is the ratio of depth to radius of the pit. The results are given in Fig. 8. This

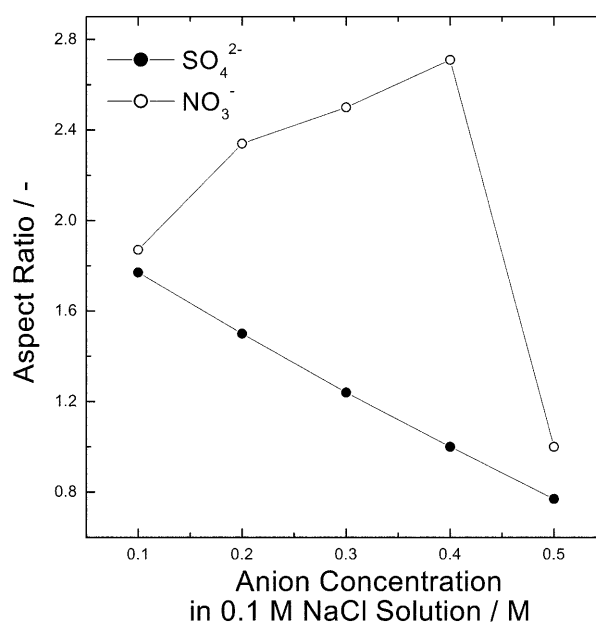


Fig. 8 Changes in the values of the aspect ratio with various anion concentrations in 0.1 M NaCl solution during artificial pit growth

clearly shows that the addition of SO_4^{2-} results in lateral growth of the pit, while the addition of NO_3^- promotes downward growth of the pit.

From the experimental findings, two types of pit growth mechanism by adding SO_4^{2-} or NO_3^- ions to NaCl solution are proposed. On the one hand, the addition of SO_4^{2-} ions accelerates the pit growth preferentially in the lateral direction. This originates from the active dissolution of Al by the attack of both SO_4^{2-} and Cl^- at the pit wall and the retardation of active dissolution of Al by the formation of $\text{Al}_2(\text{SO}_4)_3$ at the pit bottom. On the other hand, the addition of NO_3^- ions helps the pit growth preferentially in the downward direction. This can be accounted for in this way: the creation of an aggressive environment at the pit bottom owing to the lower mobility of NO_3^- than Cl^- promotes the dissolution of Al at the pit bottom.

Conclusions

Potentiodynamic polarization curves show a rise in E_{pit} values upon increasing SO_4^{2-} or NO_3^- ion concentrations in chloride solution, implying inhibition of pit initiation. However, as the SO_4^{2-} ion concentration increases, the steady-state current density increases at potentials above E_{pit} . This suggests that the addition of SO_4^{2-} ions to NaCl solutions enhances pit growth.

In the presence of SO_4^{2-} ions, the value of the average pit current obtained from potentiostatic current transients of artificial pits rises with increasing SO_4^{2-} ion concentration, indicating that the pit grows more rapidly in SO_4^{2-} -containing NaCl solution than in SO_4^{2-} -free NaCl solution. Moreover, from observations of the morphologies of the pits, it was found that pits grow preferentially in the lateral direction.

In the presence of NO_3^- ions, the value of the average pit current increases up to a NO_3^- ion concentration around 0.4 M and then decreases abruptly with increasing NO_3^- ion concentration, indicating that the pit

grows more rapidly with a NO_3^- ion concentration up to 0.4 M and the pit growth is retarded at a NO_3^- ion concentrations above 0.4 M. From the cross-sectional views of the artificial pits, the pit was observed to grow preferentially in the downward direction up to a NO_3^- ion concentration of 0.4 M.

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References

- Hunter MS (1970) *J Electrochem Soc* 117:1215
- Dunn CG, Bolon RB, Alwan AS, Stirling AW (1971) *J Electrochem Soc* 118:381
- Alwitt RS, Uchi H, Beck TR, Alkire RC (1984) *J Electrochem Soc* 131:13
- Böhni H, Uhlig HH (1969) *J Electrochem Soc* 116:906
- Rudd WJ, Scully JC (1980) *Corros Sci* 20:611
- McCafferty E (1990) *J Electrochem Soc* 137:3731
- Brett CMA, Gomes IAR, Martins JPS (1994) *Corros Sci* 36:915
- Kliskic M, Radosevic J, Gudic S (1997) *J Appl Electrochem* 27:947
- Kolics A, Polkinghorne JC, Wieckowski A (1998) *Electrochim Acta* 43:2605
- Pyun S-I, Moon S-M (1999) *J Solid State Electrochem* 3:331
- Reiser DB, Alkire RC (1984) *Corros Sci* 24:579
- Alkire RC, Wong KP (1988) *Corros Sci* 28:411
- Newman RC, Franz EM (1984) *Corrosion* 40:325
- Frankel GS (1990) *Corros Sci* 30:1203
- Wong KP, Alkire RC (1990) *J Electrochem Soc* 137:3010
- Buzza DW, Alkire RC (1995) *J Electrochem Soc* 142:1104
- Park J-J, Pyun S-I, Lee W-J, Kim H-P (1999) *Corrosion* 55:380
- Isaacs HS, Cho J-H, Rivers ML, Sulton SR (1995) *J Electrochem Soc* 142:1111
- Hakkarainen TJ (1998) *Mater Sci Forum* 289–292:955
- Hunkeller F, Böhni H (1984) *Corrosion* 40:534
- Flis J, Kowalczyk L (1995) *J Appl Electrochem* 25:501
- Lee W-J, Pyun S-I (2000) *Electrochim Acta* 45:1901
- Horvath AL (1985) *Handbook of aqueous electrolyte solutions*. Wiley, New York, p 236
- Linke WF, Seidell A (1958) *Solubilities, inorganic and metal organic compounds; a compilation of solubility data from the periodical literature*. American Chemical Society, Washington, p 164, p 188, and p 204