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The inhibition mechanism of pitting corrosion of pure aluminum by nitrate and sulfate ions in neutral chloride solution

Received: 16 October 1998 / Accepted: 6 January 1999

Abstract The inhibition mechanism of pitting corrosion of natural oxide film-covered pure aluminum by NO_3^- and SO_4^{2-} ions has been examined in 0.1 M NaCl solution using potentiodynamic polarization experiments, a.c. impedance spectroscopy, Auger electron spectroscopy and a combination of the potentiostatic current transient method and optical microscopy. It was found that NO_3^- ions can be incorporated into the natural oxide film on pure aluminum at open-circuit potential, but the incorporation of SO_4^{2-} ions into the film hardly occurs. The incorporation of NO_3^- ions lowered the pitting susceptibility of pure aluminum in 0.1 M NaCl solution. Based upon the experimental results, it is suggested that the pitting corrosion inhibition mechanism by anions can be classified into two different groups: inhibition by competitive adsorption of anions (SO_4^{2-}) with Cl^- ions and inhibition by the incorporation of anions (NO_3^-) into the film rather than competitive adsorption. Both cases may impede the incorporation of Cl^- ions into the film, thus inhibiting pitting corrosion of natural oxide film-covered pure aluminum in chloride solutions.

Key words Aluminum · Pitting · Corrosion inhibition · Nitrate ion · Sulfate ion

Introduction

The effect of inhibitive anions on the pitting corrosion of aluminum in aqueous chloride solutions has been widely investigated for the purpose of the prevention of pitting

failure [1–8]. The inhibition mechanism of pitting corrosion of aluminum by inhibitive anions in chloride solutions has been mainly studied in terms of competitive adsorption of the anions [1–6] with chloride ions for sites available on the oxide film surface and formation of complexes [7, 8]. Bohni and Uhlig [1] reported that NO_3^- and SO_4^{2-} ions retard the initiation of pits in chloride solutions. In previous work [8] it was suggested that NO_3^- ions may be incorporated under applied anodic potential in alkaline solution, thus contributing to the inhibition of pitting corrosion of pure aluminum. At present, however, it is still open to assert a mechanism of the inhibition of the pitting corrosion of aluminum by NO_3^- and SO_4^{2-} ions in chloride solutions.

It is generally agreed that pits are initiated by the incorporation of aggressive anions into the oxide film on aluminum rather than by the adsorbed anions themselves [6, 9–12]. Thus, the efficiency of inhibition by inhibitive anions may be determined by how the inhibitive anions can retard the incorporation of aggressive anions into the film. Since the adsorption is a primary step for the incorporation of aggressive anions, inhibitor anions can retard the incorporation of aggressive anions by a competitive adsorption mechanism. In addition, the incorporation of aggressive anions may be influenced by the change in the film resistance arising from the incorporation of inhibitor anions. Thus, it is of importance first to determine whether inhibitor anions could be incorporated into the surface film, and the next step is to establish if a relationship exists between the incorporated anions and the pitting resistance.

In the present work, the inhibition mechanism of pure aluminum by two inhibitor anions, nitrate and sulfate, has been examined in 0.1 M NaCl solution. For this purpose, we employed potentiodynamic polarization experiments, a.c. impedance spectroscopy, Auger electron spectroscopy and finally the combination of the potentiostatic current transient method and optical microscopy, and we discuss the experimental results obtained in terms of the adsorption and incorporation of the inhibitive anions.

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Experimental

In this work, two kinds of electrode specimens were employed. One was made of 99.999 purity aluminum rod (Aldrich) of 6.35 mm diameter, and the other was made of 99.99 purity thin aluminum film deposited by sputtering on a silicon wafer. The rod electrode was set in a block of polyethylene and the upper surface of the block was ground with silicon carbide papers successively up to 2000 grit. Both the rod and the thin film electrodes were previously immersed in distilled water for 2 h to obtain the natural oxide film on pure aluminum (the first step of pre-immersion). After that, the natural oxide film-covered pure aluminum rod and thin film specimens were immersed in 1 M NaNO₃ solution or 1 M Na₂SO₄ solution for various immersion times (10 min to 2 h) (the second step of pre-immersion). The pure aluminum rod and thin film specimens, prepared by one or two steps of pre-immersion treatment, were used for the electrochemical experiments with optical microscopy and for the analyses of Auger electron spectra, respectively.

The electrolytes used in this study were aerated 0.1 M NaCl, 0.1 M NaCl + 0.1 M NaNO₃, 0.1 M NaCl + 0.1 M Na₂SO₄, 1 M NaNO₃ and 1 M Na₂SO₄ solutions. In all the electrochemical experiments a platinum gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All the experiments were conducted at ambient temperature.

Potentiodynamic polarization experiments were conducted on the pure aluminum rod specimen, previously immersed in distilled water for 2 h (one pre-immersion step), with a scan rate of 1 mV s⁻¹ in 0.1 M NaCl, 0.1 M NaCl + 0.1 M NaNO₃ and 0.1 M NaCl + 0.1 M Na₂SO₄ solutions using an EG&G model 273 galvanostat/potentiostat.

A.c. impedance measurements were made on the pure aluminum rod specimen, previously immersed in distilled water for 2 h (one pre-immersion step), with immersion time in 1 M NaNO₃ and 1 M Na₂SO₄ solutions using a Zahner IM5D impedance analyzer by superimposing an a.c. signal of 5 mV_{rms} amplitude on open-circuit potential over 0.1–10⁵ Hz. The impedance measurements were also performed at open-circuit potential in 0.1 M NaCl solution on the pure aluminum rod specimen, previously immersed in distilled water for 2 h and then immersed in 1 M NaNO₃ or 1 M Na₂SO₄ solution for 30 min (two pre-immersion steps).

Potentiostatic current transient was obtained from the pure aluminum rod specimen, previously immersed in distilled water for 2 h and then immersed in 1 M NaNO₃ or 1 M Na₂SO₄ solution for various immersion times (two pre-immersion steps), by jumping the open-circuit potential to -0.5 V_{SCE} in 0.1 M NaCl solution. After the potentiostatic current transient experiments, optical micrographs of the pitted surface of the pure aluminum rod specimen were obtained.

Auger electron spectra were obtained from the pure aluminum thin film specimen, previously immersed for 2 h in distilled water and then immersed in 1 M NaNO₃ and 1 M Na₂SO₄ solutions for 1 h (two pre-immersion steps) using a Perkin Elmer model PHI 4300 Auger electron spectrometer equipped with a sputter ion gun. The primary electron beam has an accelerating voltage of 5 keV and an adsorbed current of 0.3 μA. The electron beam diameter at the target was about 2 μm. The modulation amplitude of the phase sensitive detector was set at 4 eV peak to peak. Under these conditions, the Auger electron spectrum was recorded with a scan rate of 6 eV s⁻¹.

Results and discussion

Inhibition effect of pitting corrosion by NO₃⁻ and SO₄²⁻ ions

Figure 1 shows potentiodynamic polarization curves obtained from the pure aluminum rod specimen, previ-

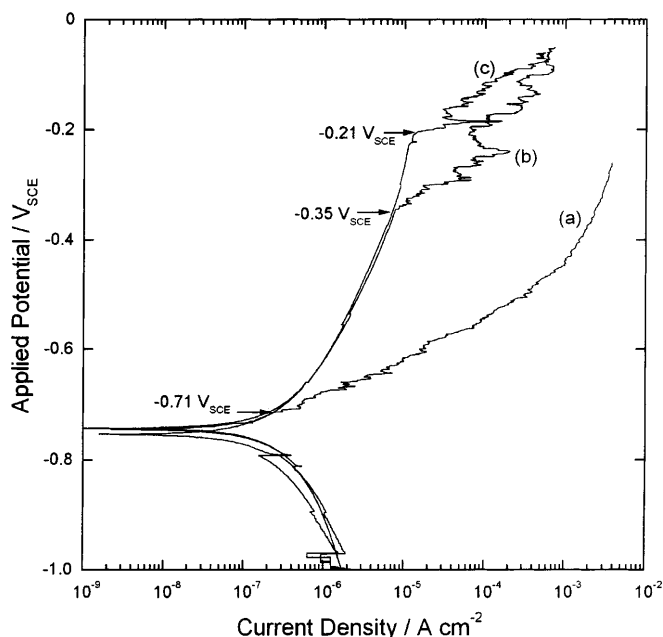


Fig. 1 Potentiodynamic polarization curves obtained from the pure aluminum rod specimen with a scan rate of 1 mV s⁻¹ in (a) 0.1 M NaCl, (b) 0.1 M NaCl + 0.1 M NaNO₃ and (c) 0.1 M NaCl + 0.1 M Na₂SO₄ solutions. The rod specimen was previously immersed in distilled water for 2 h (one pre-immersion step)

ously immersed in distilled water for 2 h, in 0.1 M NaCl, 0.1 M NaCl + 0.1 M NaNO₃ and 0.1 M NaCl + 0.1 M Na₂SO₄ solutions. The pitting potential was observed to be about -0.71 V_{SCE} in 0.1 M NaCl, which is slightly lower than the -0.67 V_{SCE} and -0.685 V_{SCE} reported by Broli and Holtan [13] and McCafferty [14], respectively. Considering that they [13, 14] used a surface pre-treatment of etching in alkaline solutions in which a relatively thicker surface oxide film may be developed, a slightly lower pitting potential obtained in this work is attributable to a comparatively thinner natural oxide film generated on pure aluminum in distilled water.

The pitting potential shifted to more positive values of -0.35 V_{SCE} and -0.21 V_{SCE} by the addition of NO₃⁻ and SO₄²⁻ ions to 0.1 M NaCl solution, respectively. It is known [1] that these anions, which do not of themselves cause pitting, shift the pitting potential in the positive direction corresponding to improved pitting corrosion resistance. Thus, it can be said that the initiation of pits is inhibited by both NO₃⁻ and SO₄²⁻ ions. The higher value of the pitting potential in the presence of SO₄²⁻ ions than that in the presence of NO₃⁻ ions suggests that SO₄²⁻ ions are more effective than NO₃⁻ ions in the inhibition of pitting corrosion of pure aluminum.

The inhibition efficiency of pure aluminum by anions in chloride solutions was investigated by Bohni and Uhlig [1]. Based upon the logarithmic relationships between the critical chloride concentration and the anion concentration in solution, they [1] reported that the efficiency of inhibition decreases in the order: NO₃⁻ > CrO₄⁻ > acetate > benzoate > SO₄²⁻. This is in

contrast to the result obtained in this work. The discrepancy may arise from the different surface pre-treatment processes of the specimen, which results in different states of the surface oxide film. The states of the surface oxide film will affect not only the adsorption by spontaneous reduction but also the incorporation of anions into the surface oxide film. Therefore, it should be clarified firstly whether NO_3^- and SO_4^{2-} ions can be incorporated into the surface oxide film at open-circuit potential, and secondly how the incorporated anions affect the inhibition of pitting corrosion.

Adsorption and incorporation of NO_3^- and SO_4^{2-} ions into the natural oxide film at open-circuit potential (E_{ocp})

Figures 2 and 3 give impedance spectra obtained from the pure aluminum rod specimen, previously immersed in distilled water for 2 h, at open-circuit potential (E_{ocp}) with immersion time in 1 M NaNO_3 and 1 M Na_2SO_4 solutions, respectively. The impedance spectra consist of one large capacitive semicircle in both the solutions. The diameter of capacitive semicircle significantly increased with increasing immersion time in the nitrate solution (Fig. 2), but it showed just a slight increase with immersion time in the sulfate solution (Fig. 3). Since the diameter of capacitive semicircle represents the resistance of the natural oxide film, it can be said that the oxide film resistance increased significantly with immersion time in the nitrate solution, but it increased only

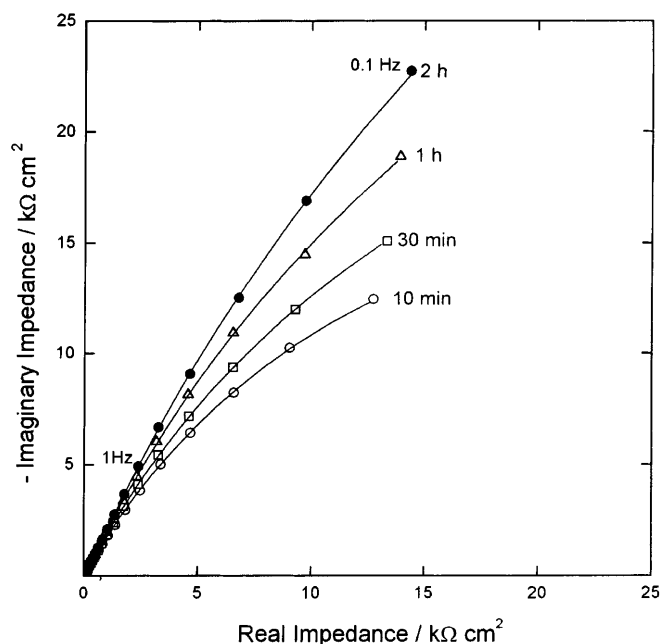


Fig. 2 Nyquist plots obtained from the pure aluminum rod specimen at open-circuit potential in 1 M NaNO_3 solution as a function of immersion time: \circ 10 min; \square 30 min; \triangle 1 h; \bullet 2 h. The rod specimen was previously immersed in distilled water for 2 h (one pre-immersion step)

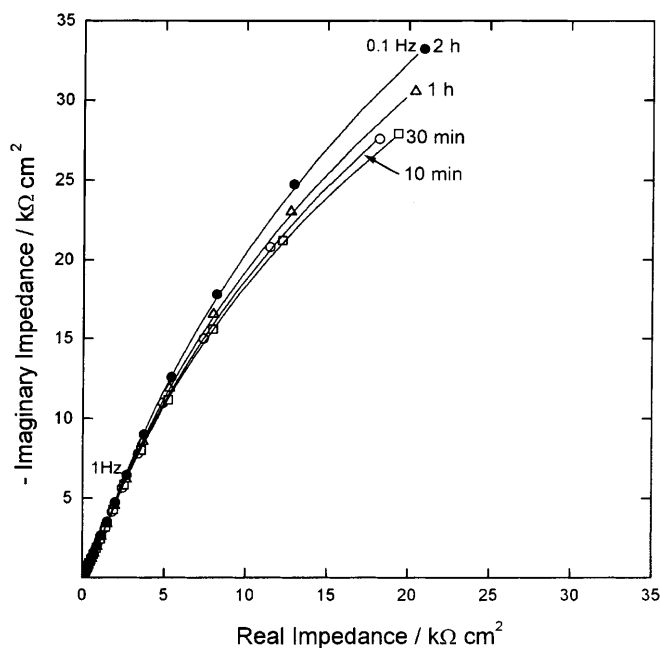


Fig. 3 Nyquist plots obtained from the pure aluminum rod specimen at open-circuit potential in 1 M Na_2SO_4 solution as a function of immersion time: \circ 10 min; \square 30 min; \triangle 1 h; \bullet 2 h. The rod specimen was previously immersed in distilled water for 2 h (one pre-immersion step)

slightly with immersion time in the sulfate solution. These reflect that NO_3^- ions can be adsorbed by spontaneous reduction and incorporated easily into the film at E_{ocp} , but the adsorption and incorporation of SO_4^{2-} ions at E_{ocp} hardly occurs.

Figure 4 demonstrates typical Auger spectra obtained after slight sputtering etching of the surface of the pure aluminum thin film specimen, previously immersed in distilled water for 2 h and then immersed in 1 M NaNO_3 and in 1 M Na_2SO_4 solutions for 1 h. As expected, the peak for nitrogen at 373 eV was observed in the case of pre-immersion in the nitrate solution. The nitrogen peak was observed at a certain position within the natural oxide film, indicating adsorption of nitrogen reduced from NO_3^- ions on the film and highly localized incorporation of NO_3^- ions into the film. However, in the case of pre-immersion in the sulfate solution, no peak for sulfur around 146 eV was observed on all the surface or in the interior of the film. This verifies that SO_4^{2-} ions cannot be adsorbed on and incorporated into the natural oxide film to appreciable amount at E_{ocp} .

Effect of incorporated NO_3^- ions on pitting corrosion

Figure 5 presents potentiostatic anodic current transients on a linear scale at an applied anodic potential of $-0.5 V_{\text{SCE}}$ in 0.1 M NaCl solution obtained from the pure aluminum rod specimen, previously immersed for 2 h in distilled water and then immersed in 1 M NaNO_3 solution for various immersion times. The anodic

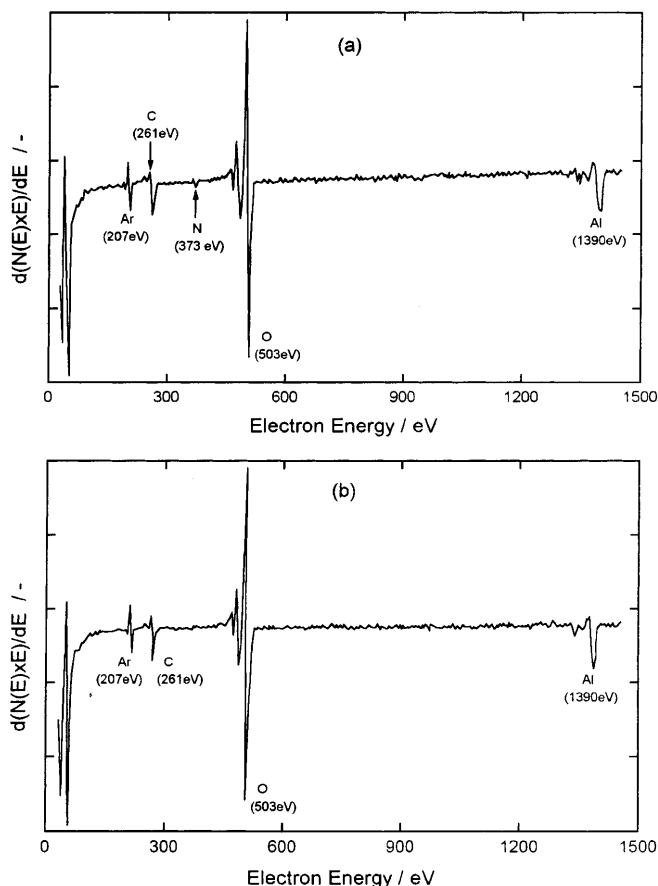


Fig. 4 Auger electron spectra obtained from the pure aluminum thin film specimen, previously immersed in distilled water for 2 h and then immersed in **a** 1 M NaNO₃ and **b** 1 M Na₂SO₄ solutions for 1 h (two pre-immersion steps)

current density i_a increased with time t . The slope of the $i_a - t$ curve in the initial stage was lowered with increasing pre-immersion time in 1 M NaNO₃ solution. This suggests that the initiation of pits is retarded by the pre-immersion treatment in nitrate solution.

Figure 6 illustrates the morphology of the pitted surface of a pure aluminum rod specimen obtained after the potentiostatic current transient experiment (Fig. 5). It is noted that the number of pits markedly decreased with increasing pre-immersion time in 1 M NaNO₃ solution. This substantiates that the initiation of pits is hindered by NO₃⁻ ion adsorption on and incorporation into the natural oxide film during the pre-immersion in nitrate solution. In addition, since the adsorbed NO₃⁻ ions seem to be incorporated into the oxide film after they cover the whole oxide film surface during the pre-immersion process, it is suggested that hindrance to the initiation of pits after pre-immersion in nitrate solution is mostly due to the incorporated part of NO₃⁻ ions into the film.

Figure 7 displays potentiostatic anodic current transients on a linear scale at an applied anodic potential of $-0.5 V_{SCE}$ in 0.1 M NaCl solution obtained from the pure aluminum rod specimen, previously im-

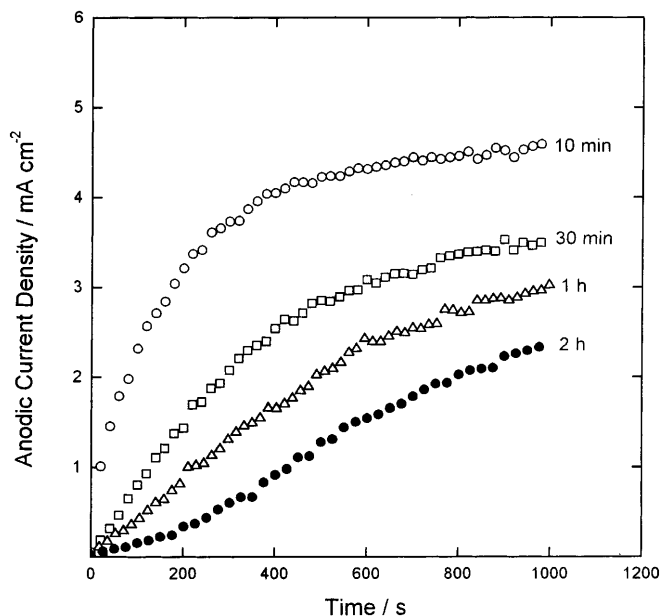


Fig. 5 Potentiostatic anodic current transients on a linear scale obtained from the pure aluminum rod specimen by jumping the open-circuit potential to $-0.5 V_{SCE}$ in 0.1 M NaCl solution. The pure aluminum rod specimen was previously immersed in distilled water and then immersed in 1 M NaNO₃ solution for: ○ 10 min; □ 30 min; △ 1 h; ● 2 h (two pre-immersion steps)

mersed for 2 h in distilled water and then immersed in 1 M Na₂SO₄ solution for various immersion times. In contrast to the case of pre-immersion treatment in nitrate solution, the slope of the $i_a - t$ curve in the initial stage was found to be independent of the pre-immersion time in sulfate solution. The number of pits was also observed to be nearly constant, irrespective of the pre-immersion time in sulfate solution. These results suggest that the pre-immersion treatment of the natural oxide film-covered pure aluminum in sulfate solution scarcely affects the initiation of pits in chloride solution.

Inhibition mechanism of pitting corrosion by NO₃⁻ and SO₄²⁻ ions

Figure 8 depicts Nyquist plots in 0.1 M NaCl solution obtained from the pure aluminum rod specimen, previously immersed in distilled water and then immersed in 1 M NaNO₃ and 1 M Na₂SO₄ solutions for 30 min. The diameter of the capacitive semicircle, which is proportional to the film resistance, was increased by pre-immersion in 0.1 M NaNO₃ solution, but it showed nearly the same value as that of the natural oxide film on the specimen prepared by pre-immersion treatment in 0.1 M Na₂SO₄ solution. It is readily inferred that the increase in the film resistance in chloride solution by pre-immersion in nitrate solution is due to the incorporation of NO₃⁻ ions into the film, as already manifested in Figs. 2 and 4a. It should be mentioned that the increased film

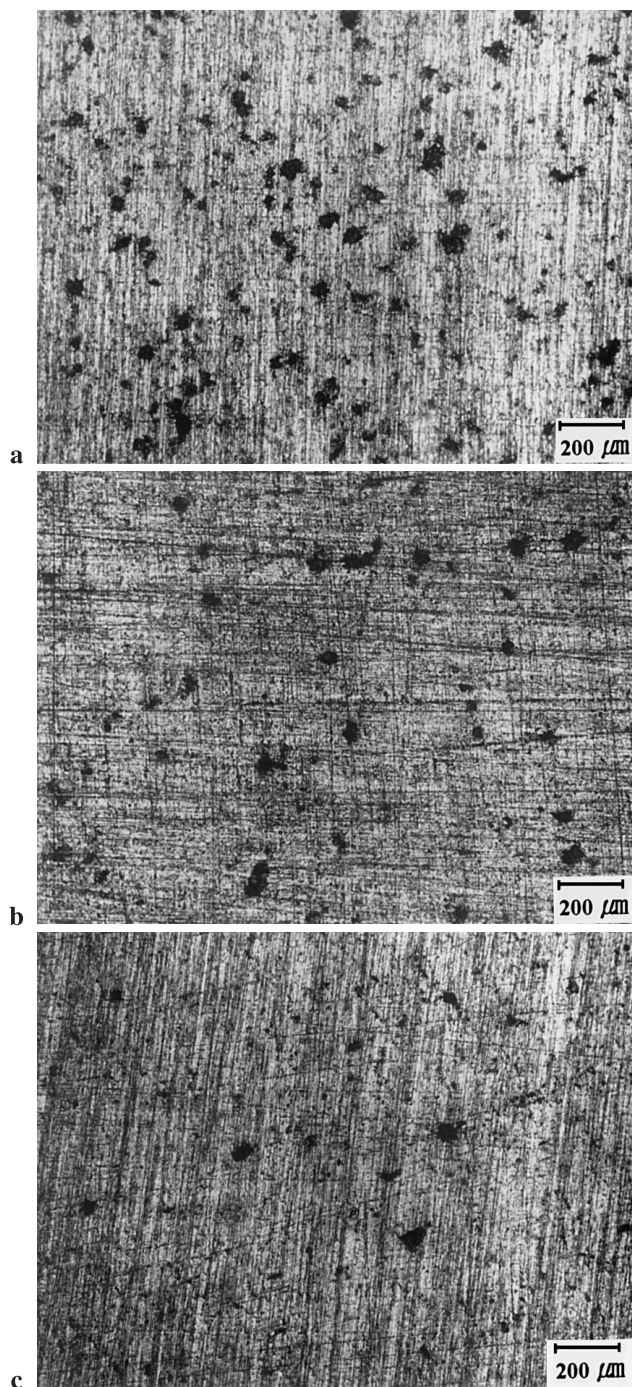


Fig. 6a-c Photomicrographs of the pitted surface obtained after applying an applied anodic potential of $-0.5 V_{SCE}$ to the pure aluminum rod specimen for 10^3 s in 0.1 M NaCl solution. The rod specimen was previously immersed in distilled water and then immersed in 1 M $NaNO_3$ solution for: **a** 0 min; **b** 30 min; **c** 1 h (two pre-immersion steps)

resistance by pre-immersion treatment in nitrate solution lowers the pitting susceptibility, as shown in Figs. 5 and 6.

Kolics et al. [6] proposed that the pitting process is initiated by the incorporation of Cl^- ions rather than by

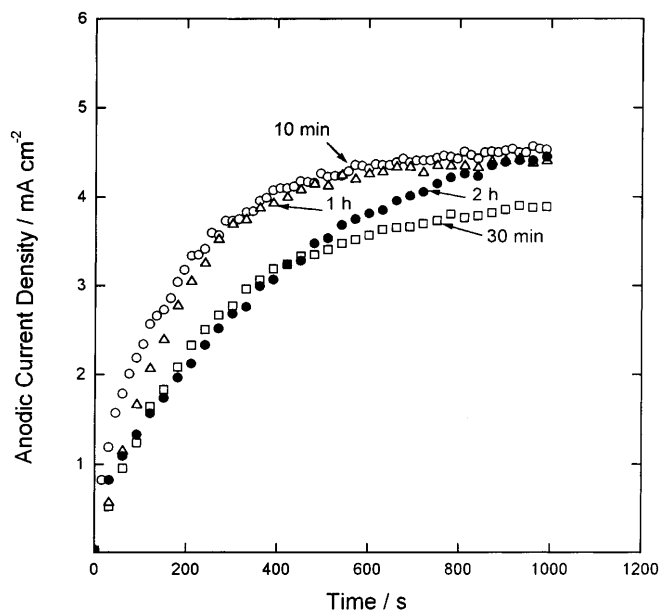


Fig. 7 Potentiostatic anodic current transients on a linear scale obtained from the pure aluminum rod specimen by jumping the open-circuit potential to $-0.5 V_{SCE}$ in 0.1 M NaCl solution. The pure aluminum rod specimen was previously immersed in distilled water and then immersed in 1 M Na_2SO_4 solution for: \circ 10 min; \square 30 min; \triangle 1 h; \bullet 2 h (two pre-immersion steps)

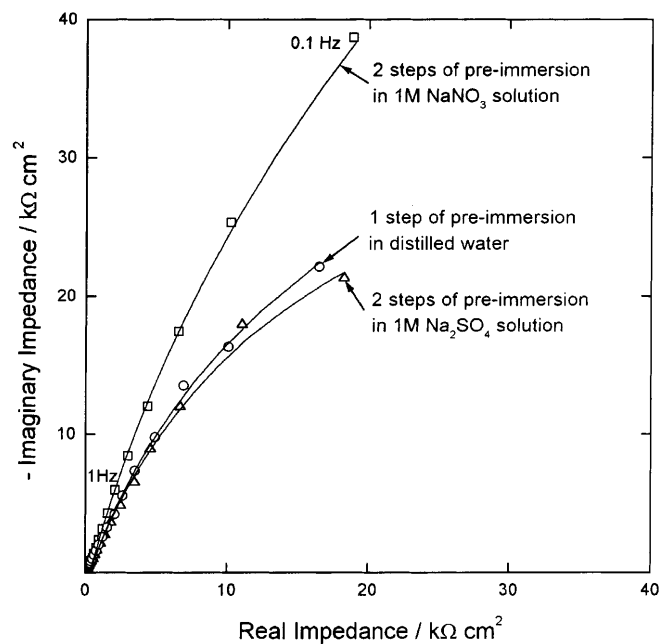


Fig. 8 Nyquist plots obtained from the pure aluminum rod specimen at open-circuit potential in 0.1 M NaCl solution. The rod specimen was previously immersed for 2 h in distilled water (\circ) (one pre-immersion step) and then immersed for 30 min in 1 M $NaNO_3$ (\square) and 1 M Na_2SO_4 (\triangle) solutions (two pre-immersion steps)

adsorbed Cl^- ions. An in-depth profile of Cl^- ions for the anodic oxide film using a Camera Ion Analyzer [10] and Auger electron spectroscopy [15] clearly showed

that Cl^- ions can be incorporated into the film. Thus, the inhibition mechanism of pitting corrosion by anions can be described by how inhibitive anions can retard the incorporation of aggressive anions into the film. There are two ways of retarding the incorporation of aggressive anions: one is to reduce the surface coverage of aggressive anions; the other is to lower the number of defect sites in the film which aggressive anions can enter. The former is a result of the competitive adsorption model [16] which has been generally employed for the explanation of the inhibition mechanism of corrosion by inhibitive anions [4, 16, 17] and organic compounds [5, 18]. The latter is a result of an incorporation model suggested in this work. The incorporation model is applicable to the explanation of pitting corrosion inhibition by NO_3^- ions in chloride solution.

Conclusions

This work explores the inhibition mechanism of pitting corrosion of the natural oxide film-covered pure aluminum by NO_3^- and SO_4^{2-} ions in 0.1 M NaCl solution using potentiodynamic polarization experiments, a.c. impedance spectroscopy, Auger electron spectroscopy and a combination of the potentiostatic current transient method and optical microscopy. The pitting potential of the natural oxide film-covered pure aluminum was significantly increased by the addition of NO_3^- and SO_4^{2-} ions to 0.1 M NaCl solution. The analyses of the a.c. impedance spectra and Auger electron spectra revealed that NO_3^- ions can be incorporated into the natural oxide film on pure aluminum at open-circuit potential, but the incorporation of SO_4^{2-} ions into the film scarcely occurs. The incorporation of NO_3^- ions was found to markedly reduce the pitting susceptibility of pure aluminum. The inhibition of pitting corrosion by SO_4^{2-} ions seems to arise from their competitive adsorption with Cl^- ions for sites available on the surface. Both the incorporation of NO_3^- ions and the competitive adsorp-

tion of SO_4^{2-} ions may retard the incorporation of Cl^- ions into the film, thereby reducing the pitting susceptibility.

Acknowledgements This work was financially supported in the period of 1997/1998 by the Korea Science and Engineering Foundation (KOSEF) through the Center for Interface Science and Engineering of Materials (CISEM). The authors are grateful to Mr. W.-J. Lee for his helpful suggestions on this paper. One of the authors (S.M.M.) is indebted to CISEM and the Corrosion & Interfacial Electrochemistry Research Laboratory (CIERL) in the Korea Advanced Institute of Science and Technology for financial support during his stay in the period of September 1997 to September 1998 at CIERL as a postdoctoral research fellow.

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