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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 $E_{\text{pit}}$ 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
role of the HCO₃⁻ ion in the morphology of a growing pit in chloride solutions has not been clearly examined.

In the present work, the effects of SO₄²⁻ and NO₃⁻ 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 SO₄²⁻ and NO₃⁻ ion additives have been proposed.

**Experimental**

The specimen used in this investigation was a 99.9999% 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 Na₂SO₄ or NaNO₃ 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 SO₄²⁻ and NO₃⁻ 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 V SCE by using an EG&G model 263A galvanostat/potentiostat. The pitting potential (Eₚₛᵦ) of pure Al in the absence of SO₄²⁻ and NO₃⁻ 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 V SCE to examine the effects of SO₄²⁻ and NO₃⁻ 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 V 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 SO₄²⁻ or NO₃⁻ 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 SO₄²⁻ and NO₃⁻ ion concentrations. All the experiments were conducted at 25 °C.

**Results and discussion**

Retardation of pit initiation by SO₄²⁻ and NO₃⁻ 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 SO₄²⁻ or NO₃⁻ ion concentrations (0, 0.1, 0.2, 0.3, 0.4 and 0.5 M). As the concentrations of SO₄²⁻ or NO₃⁻ increased, Eₚₛᵦ shifted to more positive values, indicating the impendence to pit initiation of pure Al by the addition of SO₄²⁻ or NO₃⁻ ions. This is caused by the competitive adsorption of SO₄²⁻ ions with Cl⁻ ions and by the incorporation of NO₃⁻ ions into the oxide film, respectively [10].