

## Pitting Corrosion of Aluminum Alloy in Marine Environment

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Aluminum and aluminum alloys have superior corrosion resistance because of the formation of a stable, thin oxide film on their surface. Temperature, relative humidity (RH), and surface  $\text{Cl}^-$  accumulation accelerate the corrosion of aluminum and aluminum alloys. In a marine environment, the RH and  $\text{Cl}^-$  accumulation rate are very high. In this study, the equilibrium  $\text{Cl}^-$  concentration for NaCl solutions under various RH atmospheres and the electrochemical properties for commercially pure aluminum and Al-Mg alloy in the equilibrium  $\text{Cl}^-$  solutions were investigated, and the susceptibility to pitting corrosion of commercially pure aluminum and an Al-Mg alloy in a marine environment was investigated. The equilibrium  $\text{Cl}^-$  concentration decreased with an increase in the RH. The equilibrium relationship between the RH and the  $\text{Cl}^-$  concentration was fitted to a straight line. The pitting potentials decreased with an increase in the  $\text{Cl}^-$  concentration. At low  $\text{Cl}^-$  concentrations, the maximum open-circuit potential for pure aluminum remained constant and was lower than the pitting potential. On the other hand, at high  $\text{Cl}^-$  concentrations, the maximum open-circuit potential was slightly lower than the pitting potential and decreased with an increase in the  $\text{Cl}^-$  concentration. The maximum open-circuit potential of the Al-Mg alloy decreased with an increase in the  $\text{Cl}^-$  concentration but did not exceed the pitting potential for the concentration range considered in this study. On the basis of these observations, we derived a relationship between the RH and the electrode potential.

**Keywords:** *pitting corrosion, marine environment, relative humidity, pure aluminum, Al-Mg alloy*

### 1. Introduction

Aluminum and aluminum alloys have superior corrosion resistance because of the formation a stable, thin oxide film on their surface. Temperature, relative humidity (RH), and surface chloride ion ( $\text{Cl}^-$ ) accumulation accelerate the corrosion of aluminum and aluminum alloys. In a marine environment, the relative humidity and  $\text{Cl}^-$  accumulation rate are very high. In such environments, the corrosion resistance of aluminum and aluminum alloys may decrease, and pitting corrosion tends to occur. Hence, we investigate the susceptibility to the pitting corrosion of commercially pure aluminum and Al-Mg alloys in a marine environment. Generally, Al-Mg alloys are regarded to show relatively high corrosion resistance in marine environments. In this study, we carried out electrochemical measurements to determine why Al-Mg alloys are more corrosion resistant than pure aluminum.

### 2. Experimental

#### 2.1 Equilibrium $\text{Cl}^-$ concentration

When a  $\text{Cl}^-$  solution is started to expose to an atmosphere with constant temperature and constant RH, water ( $\text{H}_2\text{O}$ ) will evaporate from the solution or will be absorbed in the solution until the  $\text{Cl}^-$  concentration reaches the equilibrium value. Equilibrium concentration is the concentration at which the activity of  $\text{H}_2\text{O}$  in a given solution is equal to the RH of the atmosphere to which the solution is exposed. The following tests were carried out to investigate the relationship between the equilibrium  $\text{Cl}^-$  concentration and the RH. 0.1 M NaCl solution was exposed for a sufficiently long period to a constant-temperature atmosphere having constant RH. Then, the weight of the solution was measured,

and the equilibrium  $\text{Cl}^-$  concentration (mol/kg- $\text{H}_2\text{O}$ ) was calculated for different values of RH (98%, 95%, 90%, 85%, 80%, and 75%). The temperature was kept at 50 °C.

## 2.2 Electrochemical properties

Electrochemical measurements were carried out to determine the open-circuit potential ( $E_{\text{OC}}$ ) and the pitting potential ( $E_{\text{PIT}}$ ). Plates made of commercially pure aluminum and Al-4.5 mass% Mg alloy were used for specimens. Each specimen was coated with an epoxy resin, except for a 10 mm × 10 mm test area. Prior to the electrochemical measurements, the resin-coated specimens were subjected to the following pretreatment: immersion in 5% NaOH at 50 °C for 30 s and 30%  $\text{HNO}_3$  at 25 °C for 60 s. A Pt plate and a Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. Tests were conducted at 25 °C in NaCl solutions of various concentrations (0.5%, 2%, 10%, and 20%).

$E_{\text{OC}}$  measurements were carried out in non-deaerated NaCl solutions for the duration of 30 min. The  $E_{\text{PIT}}$  values were determined from the anodic polarization curves obtained for deaerated solutions.

## 3. Results and discussions

### 3.1 Equilibrium $\text{Cl}^-$ concentration

The equilibrium relationship between the RH and the  $\text{Cl}^-$  concentration at 50 °C is shown in Fig. 1. The equilibrium  $\text{Cl}^-$  concentration decreased with an increase in the RH. The aforementioned equilibrium relationship is approximated by a straight line given by the following equation:

$$(\text{Cl}^- \text{ (mol/kg-H}_2\text{O)}) = -0.21 \times (\text{RH}(\%)) + 21 \quad (1)$$

### 3.2 Electrochemical properties

The anodic polarization curves obtained for commercially pure aluminum and the Al-4.5 mass% Mg alloy in NaCl solutions (0.5%, 2%, 10%, and 20%) at 25 °C is shown in Fig. 2 and 3, respectively. From the anodic polarization curves, the sudden increase in the current was indicative of the occurrence of pitting corrosion. The passive current density for pure aluminum was 1–2  $\mu\text{A}/\text{cm}^2$  which is lesser than the dissolved oxygen (DO) diffusion limited current density. The passive current density of the Al-4.5 mass% Mg alloy was approximately 10  $\mu\text{A}/\text{cm}^2$ , which is close to the DO

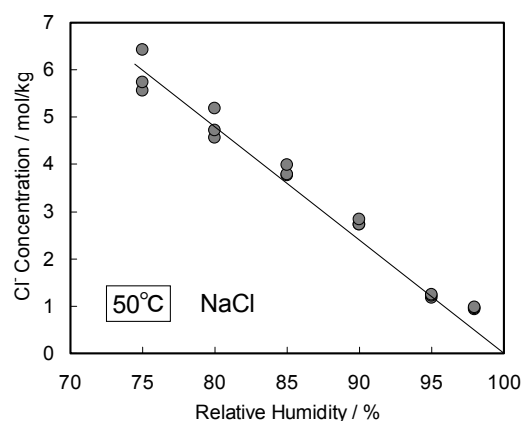


Fig. 1 Equilibrium relationship between relative humidity (RH) and  $\text{Cl}^-$  concentration at 50 °C.

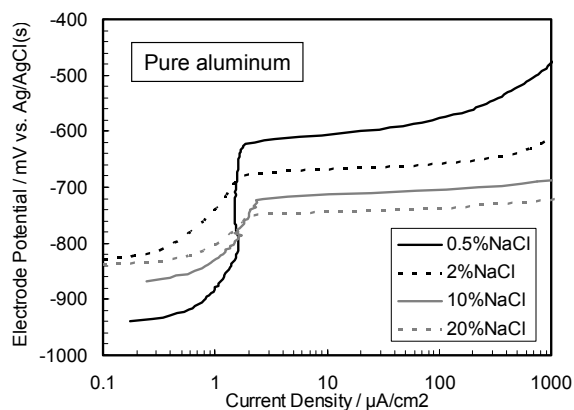


Fig.2 Anodic polarization curves for commercially pure aluminum at 25 °C.

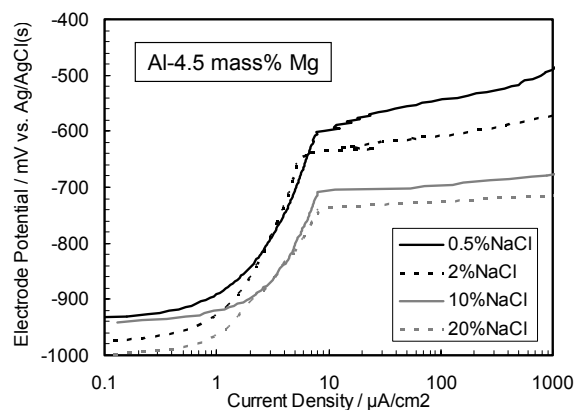


Fig.3 Anodic polarization curves for Al-4.5 mass% Mg alloy at 25 °C.

diffusion limited current density.  $E_{PIT}$  was defined as the potential at which the current density reached  $100 \mu\text{A}/\text{cm}^2$ .

The  $E_{PIT}$  values for pure aluminum were  $-560$ ,  $-640$ ,  $-700$ , and  $-730$  mV in 0.5%, 2%, 10%, and 20% NaCl solutions, respectively. The  $E_{PIT}$  values for Al-4.5 mass% Mg were  $-530$ ,  $-600$ ,  $-670$ , and  $-720$  mV in 0.5%, 2%, 10%, and 20% NaCl solutions, respectively. Thus, the  $E_{PIT}$  decreased with an increase in the  $\text{Cl}^-$  concentration.

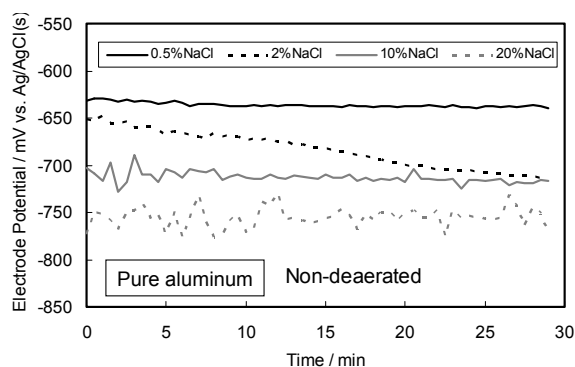


Fig.4 Time variations of open-circuit potential for commercially pure aluminum at 25 °C.

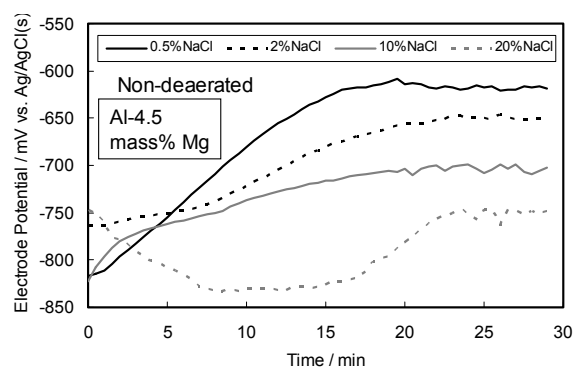


Fig.5 Time variations of open-circuit potential for Al-4.5 mass% Mg alloy at 25 °C.

The time variations of  $E_{OC}$  for commercially pure aluminum and the Al-4.5 mass% Mg alloy in NaCl solutions (0.5%, 2%, 10%, 20%) at 25 °C is shown in Fig. 4 and 5, respectively. For the case of pure aluminum in 0.5% NaCl,  $E_{OC}$  was approximately  $-630$  mV, which was 70 mV less noble than the  $E_{PIT}$  value of  $-560$  mV for this solution. In 2% NaCl,  $E_{OC}$  was initially  $-650$  mV, which is slightly lower than the corresponding  $E_{PIT}$  value, and gradually decreased to  $-710$  mV. In 10% NaCl,  $E_{OC}$  fluctuated between  $-680$  mV and  $-730$  mV, while in 20% NaCl,  $E_{OC}$  fluctuated between  $-730$  mV and  $-780$  mV. For the Al-4.5 mass% Mg alloy,  $E_{OC}$  reached steady state values of  $-610$ ,  $-650$ ,  $-700$ ,  $-750$  mV in each solutions, and these maximum values were less noble than respective  $E_{PIT}$ .

The effect of  $\text{Cl}^-$  concentration on the maximum value of  $E_{OC}$  ( $E_{OC, MAX}$ ) and  $E_{PIT}$  for pure aluminum and the Al-4.5 mass% Mg alloy is shown in Fig. 6 and 7, respectively. The  $E_{OC, MAX}$  values

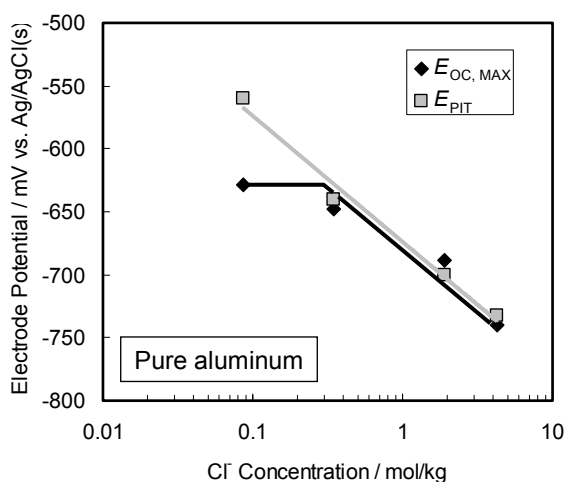


Fig. 6 Effect of  $\text{Cl}^-$  concentration on open-circuit potential and pitting potential for commercially pure aluminum.

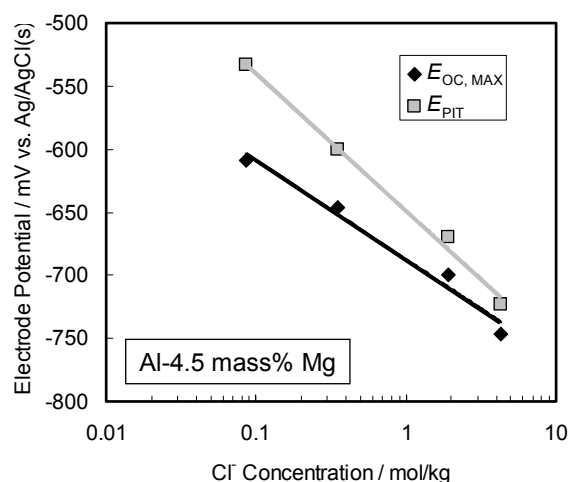


Fig. 7 Effect of  $\text{Cl}^-$  concentration on open-circuit potential and pitting potential for Al-4.5 mass% Mg alloy.

of pure aluminum remained constant at low  $\text{Cl}^-$  concentrations, where pitting corrosion did not occur. On the other hand, at high  $\text{Cl}^-$  concentrations, where pitting corrosion occurred, the  $E_{\text{OC, MAX}}$  values were slightly lower than the  $E_{\text{PIT}}$  values and decreased with an increase in the  $\text{Cl}^-$  concentration. The  $E_{\text{OC, MAX}}$  values of the Al-4.5 mass% Mg alloy decreased with an increase in the  $\text{Cl}^-$  concentration but did not become equal to the  $E_{\text{PIT}}$  values for the  $\text{Cl}^-$  concentration range considered in this study.

The relationships between the  $\text{Cl}^-$  concentration and  $E_{\text{OC, MAX}}$  or  $E_{\text{PIT}}$  are illustrated by the following equations:

$$E_{\text{OC, MAX}}^{1100} = -630 \quad (\text{Cl}^- < 0.35 \text{ mol/kg}) \quad (2)$$

$$E_{\text{PIT}}^{1100} = -99 \times \log[\text{Cl}^-] - 673 \quad (3)$$

$$E_{\text{OC, MAX}}^{5182} = -78 \times \log[\text{Cl}^-] - 687 \quad (4)$$

$$E_{\text{PIT}}^{5182} = -108 \times \log[\text{Cl}^-] - 648 \quad (5)$$

### 3.3 Relationships between RH and pitting corrosion susceptibility

The relationships between the RH and the electrode potential for pure aluminum and the Al-4.5 mass% Mg alloy are illustrated in Fig. 8 and 9, respectively. The relationships were derived from Eq. 1 to 5. Though the data in Fig. 1 was obtained at 50 °C and electrochemical measurement were conducted at 25 °C, temperature dependency of the relationship between the RH and  $\text{Cl}^-$  concentration is not so significant [1] and the qualitative error in this case can be regarded to be negligible. All the  $E_{\text{OC, MAX}}$  and  $E_{\text{PIT}}$  values increased with the RH, particularly when  $\text{RH} > 95\%$ . Pure aluminum did not have any pitting corrosion susceptibility when  $\text{RH} > 98.5\%$  because at these RH values,  $E_{\text{OC, MAX}}$  was  $-630 \text{ mV}$ , which was lower than  $E_{\text{PIT}}$ . However, pitting corrosion susceptibility was observed for pure aluminum when the RH was less than 98.5% because in this case,  $E_{\text{OC, MAX}} = E_{\text{CORR}} = E_{\text{PIT}}$ . For the Al-4.5 mass% Mg alloy, no pitting corrosion susceptibility was observed in the measured RH range, as  $E_{\text{OC, MAX}} < E_{\text{PIT}}$ . Because the Al-4.5 mass% Mg alloy had a higher passive current density than did pure aluminum,  $E_{\text{OC}}$  of the former did not tend to be ennobled up to the  $E_{\text{PIT}}$  value. Therefore, we conclude that the Al-4.5 mass% Mg alloy has higher pitting corrosion resistance than did pure aluminum.

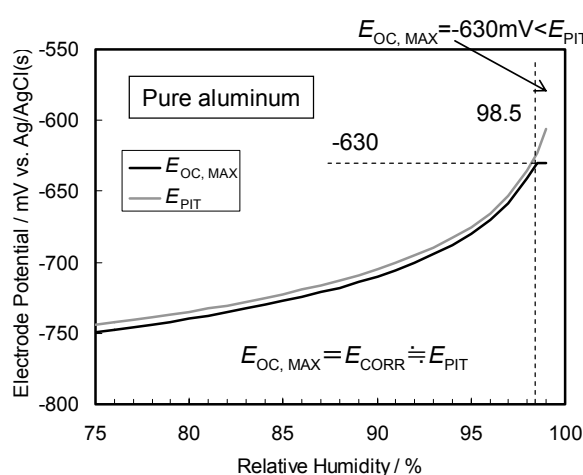


Fig. 8 Maximum open-circuit potential and pitting potential as a function of relative humidity (RH) for commercially pure aluminum.

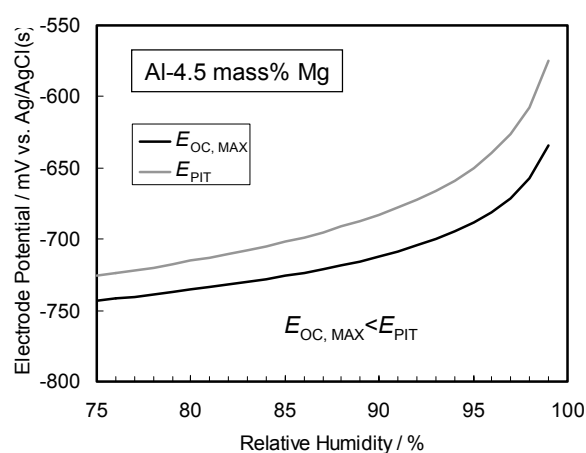


Fig. 8 Maximum open-circuit potential and pitting potential as a function of relative humidity (RH) for Al-4.5 mass% Mg alloy.

#### 4. Conclusions

1. The pitting potentials decreased with an increase in the  $\text{Cl}^-$  concentration.
2. Commercially pure aluminum was sensitive to pitting corrosion when the relative humidity was less than 98.5%.
3. The Al-Mg alloy was not sensitive to pitting corrosion in the entire RH range considered in this study.

#### References

- [1] I. Muto and K. Sugimoto, Corrosion Engineering, in Japanese, 47, (1998) 519.