

Short Communication

Influence of Magnetic Field on Corrosion Behavior of Pure Aluminum in 3.5 wt.% NaCl Solution

Xin Zhang^{1,2*}, Zehua Wang¹, Zehua Zhou¹, Guangheng Yang¹, Jing Cao¹, Xin Cai^{1*}

College of Mechanics and Materials, Hohai University, Nanjing, 210098, China
Nantong Ocean and Offshore Engineering Research Institute, Hohai University, Nantong, 226300, China

*E-mail: zhangxin.007@163.com (X. Zhang) and xcai@hhu.edu.cn (X. Cai)

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The effects of magnetic field on the corrosion behavior of pure aluminum and the properties of 3.5 wt.% NaCl solution were investigated by electrochemical measurement, pH and conductivity tests. The effects of the change of the solution properties and the magnetic field on corrosion behavior of pure aluminum were discussed. The results indicated that the corrosion sensibility and corrosion rate of pure aluminum in 3.5 wt.% NaCl solution were reduced by the magnetic field. However, magnetic field treatment could also increase pH and conductivity of NaCl solution. The change of solution properties induced by magnetic field caused the corrosion rate of pure aluminum to increase. After the magnetic field treatment was completed, the solution properties gradually recovered while the pure aluminum's corrosion rate decreased. During the corrosion process of pure aluminum, the inhibiting effect of magnetic field on the corrosion process was stronger than the promotion effect of the solution property change induced by magnetic field.

Keywords: magnetic field, corrosion behavior, magnetohydrodynamic theory, magnetization effect, magnetic memory effect

1. INTRODUCTION

With the development of marine engineering, more electronic equipment has been established in the ocean. Consequently, complex electromagnetic fields appear and impact the surrounding marine environment. Aluminum and its alloys have been widely applied in marine engineering due to their excellent comprehensive properties including good electrical properties, high corrosion resistance, and high specific strength. However, as a serious problem in marine environment, corrosion of aluminum alloys has caused a lot of economic losses and safety hazards. The presence of magnetic field in the ocean will complicate the corrosion behavior of aluminum and its alloys.

The influence of magnetic field on corrosion behavior of metals has been widely studied[1-7]. Magneto-hydrodynamic theory is usually used to explain the effect of magnetic fields on the corrosion behavior of metals[8-10]. The magnetic field impacts corrosion system of metals by introducing additional forces on the moving ions in solution[11]. When magnetic field is applied on the corrosion system, Lorentz force, the paramagnetic gradient force and the gradient magnetic force are induced. Since the influence of paramagnetic gradient force on mass transport is negligible, the effects of magnetic field on the corrosion system are mainly due to the gradient magnetic force and the Lorentz force[12-13].

The studies on ferromagnetic electrodes and electro-deposition metals were focused on the influence of magnetic field on corrosion behavior of metals. The effects of magnetic field on the dissolution of steel have been reported in many controversial studies[4,13-16]. The application of magnetic field accelerated the corrosion rate of titanium alloy and copper alloy in low-concentration NaCl solution and slowed down the corrosion behavior of zinc alloy and copper alloy in HNO₃[6-7,17]. The effect of magnetic field on corrosion behavior of aluminum and its alloys were rarely reported. Meanwhile, the reports on the corrosion behavior of aluminum were mostly focused on the additional forces induced by magnetic field. However, magnetic field can also cause the properties of corrosive solution to alter. Thus corrosion process of metals in the solution treated by magnetic field was different. The effect of the changes in the corrosive solution properties under the application of magnetic field on the corrosion process of metals was ignored in the existing studies.

In this paper, the effects of magnetic field on the properties of 3.5 wt.% NaCl solution and the corrosion behavior of pure aluminum were investigated. The effects of both the change in the solution properties and the additional force induced by magnetic field on the corrosion behavior of pure aluminum were discussed and compared.

2. EXPERIMENTAL

Experimental pure aluminum and 3.5 wt.% NaCl solution were used in the electrochemical tests. The aluminum sample sizes were 10 mm×10 mm×10 mm. The surface of samples was polished to a mirror surface by polishing cloth. Magnetic field treatment (MFT) was applied to change the properties of NaCl solution with the device in Fig. 1. When the properties of NaCl solution were stabilized, the magnetic field treatment was stopped. The properties of NaCl solution were tested after magnetic field treatment (AMFT). The properties of NaCl solution were measured by DDSJ-307 conductivity meters and PHS-3C pH meter during MFT and AMFT.

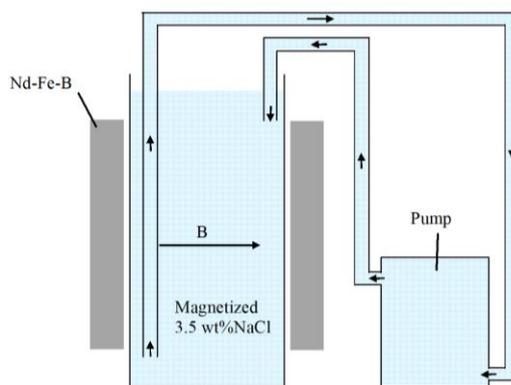


Figure 1. Test device for magnetic field treatment.

Six groups of the corrosive solution, i.e., original solution and MFT solution, original solution and MFT solution under a 0.4 T magnetic field, and 6-hour and 12-hour AMFT solutions, were prepared for the electrochemical test. The corrosion process was evaluated by a PARSTAT 2273 electrochemical workstation. A three-electrode system was used in the test. The test sample was used as the working electrode, a 232 model saturated calomel electrode was used as the reference electrode, and a 213 model Pt wire was used as the auxiliary electrode. The magnetic field with the intensity of 0.4 T was applied by a Nd-Fe-B permanent-magnet, as shown in Fig. 2. After the open circuit potential (OCP) was steady, the EIS test was performed by applying a sinusoidal potential excitation at the OCP. The sinusoidal potential had the amplitude of 5 mV and the frequency range of 10^5 to 10^{-2} Hz. The potentiodynamic polarization curves were recorded at a sweep rate of $1 \text{ mV}\cdot\text{s}^{-1}$. All measurements were repeated at least three times to ensure the accuracy of the test results.

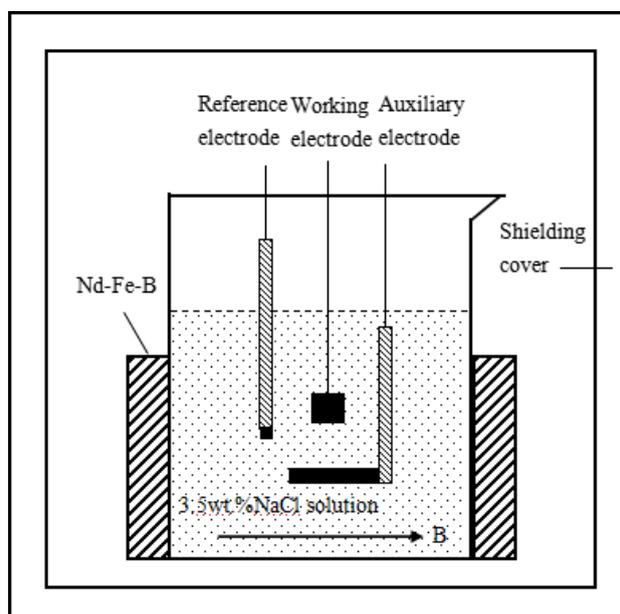


Figure 2. Device for electrochemical test.

3. RESULTS AND DISCUSSION

Fig. 3 shows the potentiodynamic polarization curves and Nyquist diagram of pure aluminum in 3.5 wt.% NaCl solution under the magnetic fields with the intensities of 0 T and 0.4 T. There was only one capacitive impedance arc in Nyquist diagram. The capacitive loop was due to the charge transfer reaction in the electric double layer formed in the corrosive solution near the metal sample, which can be described by the charge transfer resistance (R_t) and the oxide-layer capacitance of the original flat surface (C). Therefore, the EIS curve can be expressed by an equivalent circuit shown in Fig. 4. The corrosion current density (i_{corr}), corrosion potential (E_{corr}), charge transfer resistance (R_t) and the oxide-layer capacitance of the original flat surface (C) were calculated and listed in Table 1.

The applied magnetic field with the intensity of 0.4 T caused E_{corr} to shift toward positive direction from -0.8810 V to -0.8695 V. Under the 0.4 T magnetic field, the corrosion current density (i_{corr}) of the pure aluminum was $0.5232 \mu\text{A}\cdot\text{cm}^{-2}$, which was lower than that of pure aluminum tested without magnetic field ($0.8933 \mu\text{A}\cdot\text{cm}^{-2}$). At the same time, under 0.4 T magnetic field, the capacitive circle and the charge transfer resistance (R_t) of the pure aluminum were both larger than the results without magnetic field. Therefore, the application of 0.4 T magnetic field could reduce corrosion sensibility and corrosion rate of pure aluminum in 3.5 wt.% NaCl solution.

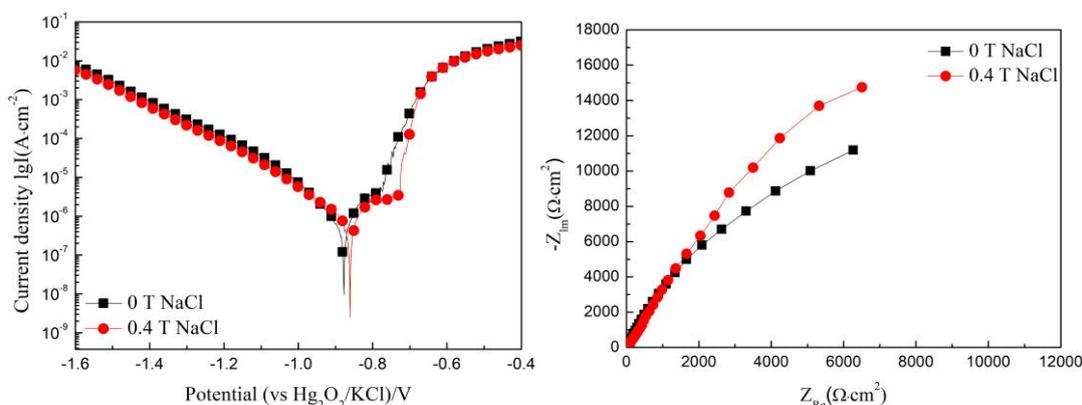


Figure 3. Potentiodynamic polarization curves and Nyquist diagram of pure aluminum in 3.5 wt.% NaCl solution with and without the application of 0.4 T magnetic field.

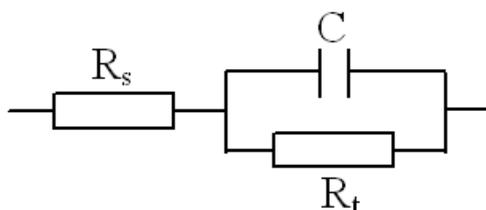


Figure 4. An equivalent circuit for pure aluminum

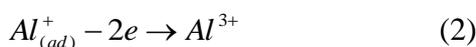
Table 1. E_{corr} , i_{corr} and E_{pit} values and equivalent elements parameters of pure aluminum calculated from the polarization curves and equivalent circuit

| | E_{corr}/V | $i_{corr}/\mu A \cdot cm^{-2}$ | $R_s/(\Omega \cdot cm^2)$ | $C/(F \cdot cm^2)$ | $R_t/(\Omega \cdot cm^2)$ |
|-------|--------------|--------------------------------|---------------------------|------------------------|---------------------------|
| 0 T | -0.881 | 0.893 | 1.162×10^5 | 7.581×10^{-6} | 3.624×10^4 |
| 0.4 T | -0.870 | 0.523 | 1.999×10^5 | 8.135×10^{-6} | 4.697×10^4 |

Oxidation (anodic reaction) and oxidant reduction (cathodic reaction) are the two associated charge transfer reactions in the corrosion of metals. Under the application of magnetic field, the magnetohydrodynamic (MHD) flow on aluminum/solution interface influenced the mass transfer and changed the activating/dissolving of aluminum anode in 3.5 wt.% NaCl solution, which can explain the effect of magnetic field on the electrode process of pure aluminum. The MHD flow in electrochemical system can be described as $\vec{F}_{MHD} = \vec{J} \times \vec{B}$, where \vec{J} is the local flux of ions.

In the electrochemical system, the moving direction of ion flux is usually determined by the direction of electronic field. Thus the direction of magnetic field is very important to the mass transfer rate in corrosion process. When the applied magnetic field is perpendicular to the direction of electronic field and ion flux, \vec{F}_{MHD} can achieve the largest value. In addition, an additional Lorentz force is also introduced by magnetic field, which moves the charged particles through the interfacial diffusion layer.

Aluminum anodic dissolution can be described in two reactions[18-19]. At first, aluminum is dissolved and loses electrons, while the active intermediate ions, i.e., $Al^{+}_{(ad)}$ are formed. The unstable $Al^{+}_{(ad)}$ ions are easily to loss electrons and become Al^{3+} ions. Then Al^{3+} and $Al^{+}_{(ad)}$ ions react with O_2 , H_2O and Cl^- to decompose the anode and destroy the passive film. The movement of electrons and the recombination of ions are involved in the corrosion process of pure aluminum. The consumption of Al^{3+} is considered as the main cause to actively maintain corrosion progress.



Magnetic fields influence the motion of cations and anions. The effect of magnetic fields on paramagnetic ions is called “paramagnetic gradient force”, which is shown in Equation (3)[11, 20-21]. In the electrode reaction, the magnetic field produces additional driving force acting on paramagnetic ions, causing the concentration gradient of the paramagnetic ions. This additional force is in the same direction as the gradient of paramagnetic ions. The additional force causes the redistribution of paramagnetic ions in the diffusion layer and increases concentration of paramagnetic ions.

$$\vec{F}_{\nabla c} = \frac{\chi_m B^2}{2\mu_0} \vec{\nabla} c \quad (3)$$

The electron configuration of $Al^{+}_{(ad)}$ ion is $1S^2 2S^2 2P^6 3S^1 3P^1$. It has a single electron in the orbits of 3S and 3P, respectively. Thus $Al^{+}_{(ad)}$ ion is a paramagnetic ion, which can be attracted by the magnetic field and accumulate on the surface of aluminum electrode. During the corrosion process of pure aluminum in 3.5 wt% NaCl solution, $Al^{+}_{(ad)}$ ions are formed, and then under the paramagnetic gradient force, the concentration of $Al^{+}_{(ad)}$ ions on the aluminum electrode surface continues to

increase. As a result, the progress of reaction (1) is hindered and the formation of Al^{3+} ions is reduced. Therefore, the magnetic field decreases the concentration of ions in the diffusion layer, and decreases the corrosion sensibility and corrosion rate of pure aluminum.

The discussion above is mainly based on the magnetohydrodynamic theory, which is focused on the effect of the additional forces induced by magnetic field on the corrosion behavior. However, the effect of magnetic field on the properties of corrosive solution should also be considered, which leads to a different corrosion behavior of pure aluminum in the MFT solution.

Fig. 5 shows the variation of pH and conductivity of 3.5 wt.% NaCl solution during and after the magnetic field treatment of with the intensity of 0.4 T. During the magnetic field treatment, the pH and conductivity of NaCl solution first increased quickly, and then achieved stable. The results indicated that magnetization effect could cause the increase in pH and conductivity of NaCl solution. After the magnetic field treatment, the pH and conductivity of NaCl solution gradually decreased close to the value of original NaCl solution. The magnetic memory lasted for about 12 hours.

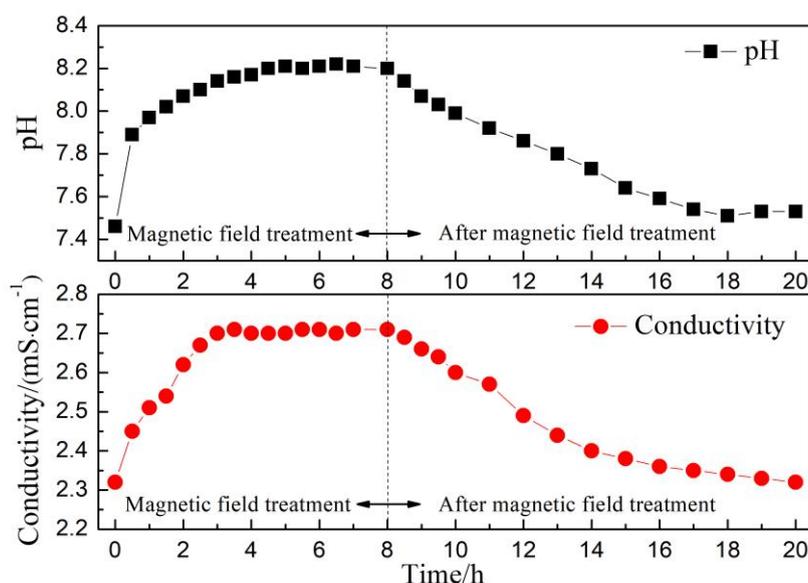


Figure 5. Variation of pH and conductivity of 3.5 wt.% NaCl solution during and after the magnetic field treatment at 0.4 T

The magnetization effect can influence the association state of the water molecules in the solvent and the hydration state of ions. The increase of the pH values during the magnetic treatment and the decrease of pH after the completion of the treatment were most probably due to the release of the CO_2 from the solutions[22]. The conductivity of electrolyte solution depends on concentration and electromobility of ions. The interaction between solvent molecules and solute ions influences the electromobility of ions and the conductivity of the solution[23]. According to ionic atmosphere theory, the central cation is surrounded by many anions, which results in the formation of ionic atmosphere with negative electricity. At the same time, many cations surrounding the central anion lead to the formation of ionic atmosphere with positive electricity. Under the electric field, the central ion and the

surrounding ionic atmosphere move in the opposite directions, which cause the relative movement of different ions. Since water is a polar medium, the ions in aqueous solution are hydrated ions [24]. The conductivity of ions decreases under the effect of electrophoresis [25]. Under magnetic field, the ionic hydration layer is destroyed, and the conductivity of aqueous solution is increased. After the magnetic field treatment is completed, it took about 12 hours for the pH and conductivity of NaCl solution to recover to the original condition. This phenomenon is called magnetic memory effect.

Fig. 6 shows the potentiodynamic polarization curves and Nyquist diagram of pure aluminum in MFT and AMFT 3.5 wt.% NaCl solution. E_{corr} , i_{corr} values and equivalent elements parameters of the pure aluminum were calculated from the polarization curves and equivalent circuit, as listed in Table 2. The E_{corr} value of pure aluminum in MFT NaCl solution was higher than that in the original solution, indicating that the MFT solution could reduce the corrosion sensibility of pure aluminum. However, the i_{corr} value of the sample in MFT solution was significantly higher than that in the original solution. The capacitive circle and the charge transfer resistance (R_t) of pure aluminum in MFT solution were both smaller than those in the original solution, indicating that the corrosion rate of pure aluminum was higher in MFT solution than in original solution. The higher corrosion rate was caused by the higher pH value and the stronger conductivity of MFT solution. In the solution with higher pH value, pure aluminum had a lower corrosion resistance[26-27]. In addition, the solution with high conductivity could accelerate the activating and dissolving processes of aluminum anode, and promote mass transfer. Therefore, magnetic field can change the properties of NaCl solution and further influence the corrosion behavior of pure aluminum in solution.

The trends of E_{corr} , i_{corr} and R_t of pure aluminum in MFT solution were also analyzed after the magnetic field treatment. With the increase of AMFT time, E_{corr} and i_{corr} decreased, while R_t increased. The corrosion parameters of pure aluminum in 12-hour AMFT NaCl solution were close to the results in the original solution. After the magnetic field treatment was completed, the properties of solution gradually recovered. After 12 hours (AMFT time was 12 hours), the properties of solution completely recovered. Therefore, with the increase of AMFT time, the corrosion rate of pure aluminum decreased to that in original solution.

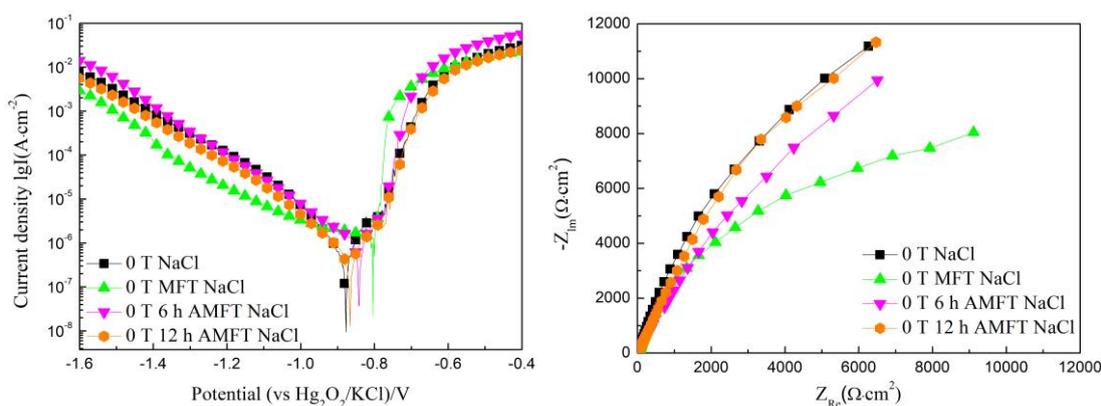


Figure 6. Potentiodynamic polarization curves and Nyquist diagram of pure aluminum in original solution, MFT solution, 6-hour AMFT solution, and 12-hour AMFT solution with 3.5 wt.% NaCl.

Table 2. E_{corr} , i_{corr} values and equivalent elements parameters of pure aluminum calculated from the polarization curves and equivalent circuit.

| | E_{corr}/V | $i_{corr}/\mu A \cdot cm^{-2}$ | $R_s/(\Omega \cdot cm^2)$ | $C/(F \cdot cm^2)$ | $R_t/(\Omega \cdot cm^2)$ |
|--------------|--------------|--------------------------------|---------------------------|------------------------|---------------------------|
| 0 T | -0.881 | 0.893 | 1.162×10^5 | 7.581×10^{-6} | 3.624×10^4 |
| 0T/MFT | -0.815 | 14.340 | 2.406×10^3 | 1.527×10^{-6} | 1.433×10^4 |
| 0T/6 h AMFT | -0.849 | 3.783 | 3.325×10^5 | 4.125×10^{-6} | 2.881×10^4 |
| 0T/12 h AMFT | -0.879 | 1.012 | 2.651×10^5 | 5.197×10^{-6} | 3.424×10^4 |

Potentiodynamic polarization curves and Nyquist diagram of pure aluminum in MFT 3.5 wt.% NaCl solution with and without the application of 0.4 T magnetic field are shown in Fig. 7. E_{corr} , i_{corr} values and equivalent elements parameters of pure aluminum were calculated from the polarization curves and equivalent circuit, as listed in Table 3. In MFT solution, the application of 0.4 T magnetic field caused E_{corr} to shift toward positive direction. The corrosion current density (i_{corr}) of pure aluminum under the 0.4 T magnetic field was lower than that without the magnetic field. At the same time, the capacitive circle and the charge transfer resistance (R_t) of pure aluminum under 0.4 T magnetic field were both bigger than those without the magnetic field. The results indicated that the application of the 0.4 T magnetic field could reduce the corrosion sensibility and the corrosion rate of pure aluminum in 3.5 wt.% NaCl solution by the above mentioned paramagnetic gradient force and magnetohydrodynamic flow.

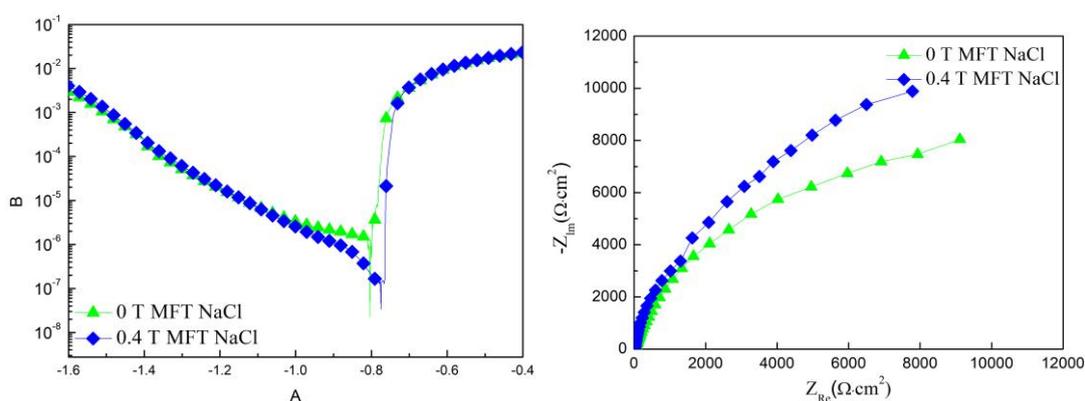
**Figure 7.** Potentiodynamic polarization curves and Nyquist diagram of pure aluminum in MFT 3.5 wt.% NaCl solution with and without the application of 0.4 T magnetic field.

Table 3. E_{corr} , i_{corr} values and equivalent elements parameters of pure aluminum calculated from the polarization curves and equivalent circuit

| | E_{corr}/V | $i_{corr}/\mu A \cdot cm^{-2}$ | $R_s/(\Omega \cdot cm^2)$ | $C/(F \cdot cm^2)$ | $R_t/(\Omega \cdot cm^2)$ |
|----------|--------------|--------------------------------|---------------------------|------------------------|---------------------------|
| 0T/MFT | -0.815 | 14.340 | 2.406×10^3 | 1.527×10^{-6} | 1.433×10^4 |
| 0.4T/MFT | -0.773 | 6.822×10^{-3} | 1.206×10^5 | 5.139×10^{-6} | 6.767×10^4 |

As described above, the corrosion resistance of pure aluminum in MFT solution was reduced. However, the application of magnetic field can improve the corrosion resistance of pure aluminum. The results indicated that, during the corrosion process of pure aluminum under magnetic field, the inhibiting effect of magnetic field on the corrosion process by paramagnetic gradient force and magnetohydrodynamic flow was stronger than the promotion effect of the solution property change induced by the magnetic field.

4. CONCLUSION

(1) Magnetic field could reduce the corrosion sensibility and corrosion rate of pure aluminum in 3.5 wt.% NaCl solution by paramagnetic gradient force and magnetohydrodynamic flow.

(2) During the MFT (magnetic field treatment) process, both pH value and conductivity of 3.5 wt.% NaCl solution first increased quickly, and then achieved stable. Thus MFT could increase both pH and conductivity of the NaCl solution. After the magnetic field treatment was completed, the pH value and conductivity of NaCl solution gradually decreased to the values of original NaCl solution in about 12 hours.

(3) The MFT could reduce the corrosion sensibility and increase corrosion rate of pure aluminum 3.5 wt.% NaCl solution by increasing the pH value and conductivity of solution. After the magnetic field treatment was completed, the corrosion rate of pure aluminum gradually decreased to the value in the original solution.

(4) During the corrosion process of pure aluminum under the application of magnetic field, the inhibiting effect of magnetic field on corrosion process by paramagnetic gradient force and magnetohydrodynamic flow was stronger than the promotion effect of solution property change induced by magnetic field.

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