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Effect of Magnetic Field on the Corrosion Behaviour of Carbon Steel in Static Seawater

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We investigated the effect of magnetic field on the corrosion behaviour of carbon steel in static seawater using finite element electrochemical simulations and electrochemical experiments. We observed that by changing the magnetic field strength and orientation, we can control the corrosion behaviour of carbon steel. Carbon steel is a magnetic material. We observed the effect of magnetic gradient force, which was introduced by self-magnetization, on the corrosion behaviour except for the Lorentz force. The analysis results indicate that the introduced magnetic gradient force is essential for inhibiting the corrosion behaviour of carbon steel. These results demonstrated that the effect of magnetization cannot be ignored during the electrochemical corrosion process of magnetic materials.

Keywords: Iron, Magnetic field, Corrosion, Seawater

1. INTRODUCTION

Seawater is the most corrosive natural environment [1]. Specifically, the damage to marine facilities cannot be ignored, because it hinders the rapid development of marine engineering. Metals are essential engineering materials in marine facilities. However, metals can be corroded by seawater, which has considerable implications for the development of global economy and marine biosafety [2]. Therefore, metal corrosion protection technology is vital [3].

Carbon steel is widely used in marine facilities and engineering owing to the cost performance advantage in corrosion resistance [4]. Therefore, the anti-corrosion studies of carbon steel in seawater are essential for marine engineering [5]. To inhibit the corrosion behaviour of carbon steel in seawater, researchers proposed many technical solutions, which are based on numerical simulations and electrochemical experiments [6-10].

Recently, it has been discovered that the corrosion behaviour of metals in seawater environments can be affected by magnetic field [11-24]. Because magnetic field does not pollute the marine environment, it is conducive to the green development of marine resources. As early as 1995, Tacken and Janssen preliminarily studied the effect of magnetic field on reaction kinetics by the theoretic modelling of mass transfer in magneto-electrolytic cells; they predicted that magnetic field can affect the many processes in electrochemical cells as an extra variable [15]. Through many experimental and theoretical studies, the prediction of Tacken and Janssen was gradually confirmed, such as the effects of magnetic flux density and magnetic susceptibility in solutions on electrochemical processes [16,17], and the effects of the Lorentz and magnetic gradient forces on the electrochemical reaction [18-21]. In many corrosion behaviour studies of metals, a sodium chloride solution was typically used to simulate seawater to facilitate the experimental analysis [22-24]. However, this cannot directly reflect the real process of seawater corrosion. In addition, carbon steel is a soft magnetic material [25], and its own magnetic behaviour cannot be ignored under external magnetic field because its magnetization affects the distribution of the surrounding magnetic field [18]. There is a lack of studies on the corrosion behaviour in seawater environment that consider the magnetization effect of carbon steel [26].

In this study, the effect of magnetic field on the corrosion behaviour of carbon steel in static seawater was investigated using the finite element electrochemical simulation and electrochemical experiments with variable external magnetic field direction.

2. EXPERIMENTS

To study the effect of magnetic field on the electrochemical corrosion behaviour of carbon steel in static seawater, a 70×10×2-mm^3 A3-Q235 carbon steel specimen [6] (99.95% purity, Yangzhou Xiangwei Machinery) was used as a working electrode. All carbon steel specimens were polished with a 5000-mesh sandpaper, and the surface was washed with water and ethanol. Each carbon steel specimen was encapsulated by epoxy resin except for an effective reaction window of 10×10 mm^2. According to the standard practice for the preparation of substitute ocean water (ASTMD 1141-98), natural salt (from the Huanyu Aquarium) was dissolved in distilled water to prepare the experimental seawater with the concentration of 30 g/L and the pH value of 8.2. During the electrochemical experiments, an NdFeB magnet with a 30-mm diameter and 20-mm thickness and an approximately 255-mT magnetic field strength at the surface centre was used to conveniently change the direction of magnetic fields, and an electromagnet device (East Changing Technologies, P90-60) was used to generate a uniform magnetic field. Free corrosion potential, potentiodynamic polarization curve, and chronoamperometry were measured using the three-electrode Teflon cell method [27]. To maintain a constant pH, free corrosion potential and chronoamperometry were set at 0.02 A/cm^2 current density and -0.2 V static potential, respectively. Based on the free corrosion potential at steady state (at 3000 s), potentiodynamic polarization curves were measured in the range of -0.6 V ~ -0.8 V with a scan rate of 1 mV/s under the uniform magnetic field. A 30×30×0.3-mm^3 platinum sheet was used as the electrode, and the saturated calomel electrode was used as the reference electrode. Potential control and current measurement were realized by a Shanghai Chenhua CHI760e electrochemical analyser. To confirm the formation of corrosion intermediate on the surface of carbon steel, the composition of the intermediate product after the electrochemical experiments was analysed by X-ray diffraction (XRD, Rigaku Ultima IV, Japan) using a conventional Cu-Ka radiation source with a scanning rate of 4°/min.

3. RESULTS AND DISCUSSION

3.1. Numerical simulation of the magnetic flux density distribution on the surface of carbon steel

To investigate the effect of magnetic field (B) on the corrosion behaviour of carbon steels in the seawater, two types of different magnetic field layouts were used [i.e., perpendicular (B⊥S) or parallel (B//S) to the carbon steel electrode surface]. To describe the magnetic flux density distribution on the surface of carbon steel electrodes in two types of magnetic field distributions, separate numerical simulations were performed according to the feature distribution of the actual magnetic flux density on the surface of the NdFeB magnet using the finite element method.

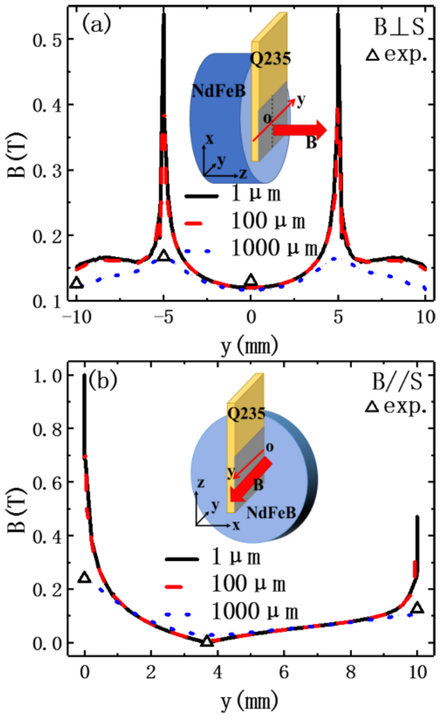

Figure 1. Distributions of magnetic flux density at the distance of 1 μm, 100 μm, and 1000 μm from the carbon steel electrode surface when (a) B⊥S and (b) B//S

The insets in Figs. 1 (a) and (b) show the magnitude of magnetic flux density along the y-direction centre lines of the carbon steel surface at distances of 1 μm, 100 μm, and 1000 μm from the surface of carbon steel. Fig. 1 (a) shows that high magnitudes and high gradients of the magnetic flux density appear symmetrically at both edges of the carbon steel sheet when the magnetic field direction is perpendicular to the surface of carbon steel. This indicates that carbon steel is a soft magnetic material [25]; the magnetic stray field will be strongest at both edges owing to the shape-dependent magnetization of carbon steel, which is similar to the case of magnetized iron in Ref. [21]. For an example, when the distance is 1 μm, the maximum magnetic flux density is ~ 0.418 T, and the average gradient is ~ 83.6 T/m at both edges. Fig. 1 (b) shows that high magnitudes and high gradients of the magnetic flux density appear at both edges of the carbon steel sheet when the magnetic field direction is parallel to the surface of carbon steel. However, we determined that the magnitudes of the magnetic flux density are asymmetric at both edges of the carbon steel sheet, which is attributed to the effect of the stray magnetic field on the surface of the NdFeB magnet. In addition, we determined that the magnitude of the magnetic flux density is close to zero at $y = 3.7$ mm; this indicates that the magnetic stray field exponentially decreased with increase in the distance from the surface of the NdFeB magnet [28]. However, from the $y = 3.7$ mm point to the other edge of the carbon steel sheet ($y = 10$ mm), the magnitude of the magnetic flux density increased again. This suggests that carbon steel, as a magnetic material, is easily magnetized by the NdFeB magnet, which works similar to magnet to generate stray fields around itself. Therefore, the carbon steel sheet behaves like a magnet. Thus, at both edges, relatively high magnetic flux densities are formed, as shown in Figs. 1(a) and 1(b).

3.2. Effect of magnetic fields on the free corrosion potential

Under two different magnetic field distributions, which are described in the above section, the free corrosion potential (U_0) of carbon steel was studied in static seawater.

To observe the effect of magnetic field on the free corrosion potential of carbon steel sheet, the NdFeB magnet was quickly brought near the carbon steel sheet, kept there for 200 s, and then quickly removed. Here, the stable free corrosion potential was the initial state without external magnetic fields. As shown in Figs. 2 (a) and (b), we observed the clear change in the free corrosion potential when the NdFeB magnet was applied and removed. The free corrosion potential decreased significantly under the magnetic field, which indicates that magnetic field inhibits the corrosion behaviour of carbon steel due to the gradient magnetic field (see Fig. 1) [19-21]. For $B\perp S$, the free corrosion potential quickly decreased by approximately 6.6 mV from -694.9 mV to -688.3 mV. However, there are some steps that may influence the instantaneous magnetic flux change of the electrochemical system, as shown in Fig. 2(a). Under the magnetic field, we determined that the free corrosion potential formed a new state of dynamic equilibrium. After the magnetic field was rapidly removed, the free corrosion potential instantly decreases again by approximately 1.6 mV, which is similar to the minimum value under the magnetic field. This observation occurs due to the influence of the instantaneous magnetic flux change on the electrochemical systems according to Lenz's law [29]. As shown in Fig. 2(b), the change profile of the free corrosion potential for B//S is 7.5 mV, which is similar to that for $B\perp S$ when the magnetic field is applied. After rapidly removing the magnetic field, the free corrosion potential decreases by approximately 0.8 mV, which is similar to that for $B\perp S$.

However, the change in the free corrosion potential for B//S is larger than that for B⊥S, which may be attributed to the effect of the Lorentz force on the corrosion behaviour of carbon steels. In addition, we determined that the free corrosion potential slowly rebounds or even returns to the original state (in two cases of B⊥S and B//S) after the quick removal of the NdFeB magnet. However, the recovery rate of the free corrosion potential for B//S is slower than that for B⊥S. We expect that the Lorentz force accelerates the ion motion [30] to produce more intermediate products, which results in the difference between the two cases.

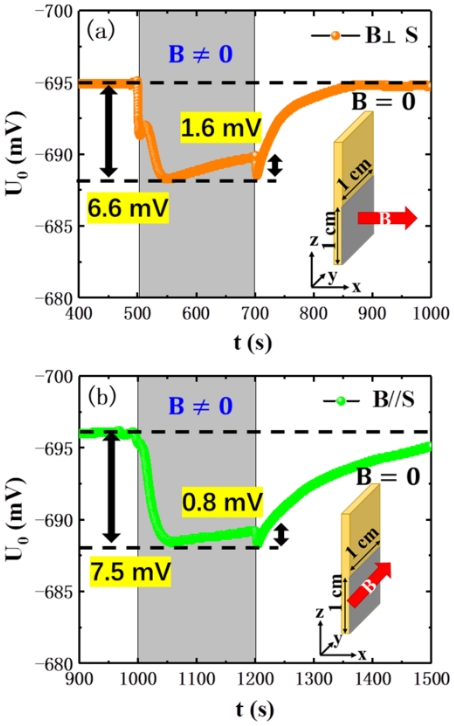

Figure 2. Effect of magnetic field on the free corrosion potential (U_0) when (a) B⊥S and (b) B//S. The insets in (a) and (b) show the magnetic field layout schematics for B⊥S and B//S.

3.3. Effect of magnetic field in chronoamperometry

To study the specific effect of magnetic field on the corrosion behaviour of carbon steel in seawater, the change in the corrosion current density (j) of carbon steel was observed under the constant potential using chronoamperometry. Here, the magnetic field in two different directions was applied. Specifically, the direction of magnetic field was perpendicular (B//E) and parallel (B⊥E) to the surface of carbon steels. After the corrosion current density of the carbon steel sheet stabilized, the NdFeB magnet was quickly attached to the carbon steel sheet and kept their for 100 s, then it was quickly removed, as shown in Figs. 3 (a) and 3 (b).

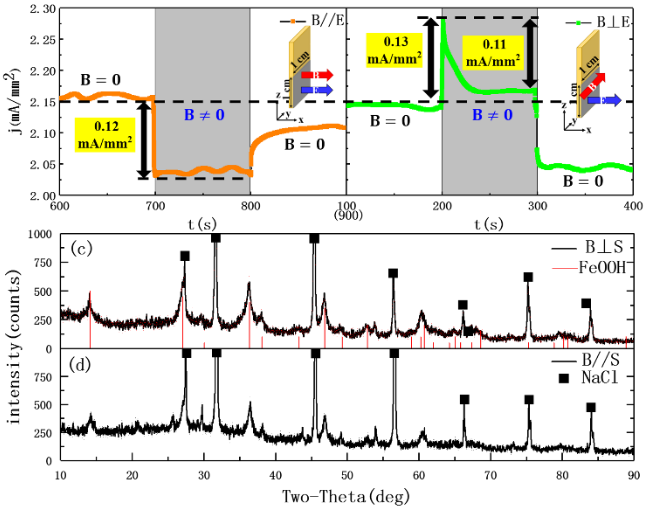

Figure 3. Change curves of the corrosion current density (*j*) for (a) B//E and (b) B⊥E. XRD profiles of the corrosion products of carbon steel for (c) B//E and (d) B⊥E

We observed that the difference in the corrosion current density curve profiles was significant when the NdFeB magnet was used for B//E and B⊥E. For B//E, the corrosion current density suddenly decreased by approximately 0.12 mA/mm^2 from ~2.15 mA/mm^2 to ~2.03 mA/mm^2 and then remained in a relatively stable state [see Fig. 3(a)] under the magnetic field. Because the magnetic field direction is parallel to the corrosion current direction, the main reason for the sudden decrease in the current density is attributed to the action of the gradient force of the magnetic field. However, for B⊥E, the corrosion current density suddenly increased by approximately 0.13 mA/mm^2 from ~2.15 mA/mm^2 to ~ 2.28 mA/mm^2 and then slowly decreased by approximately 0.11 mA/mm^2 during 40 s and remained stable at ~2.17 mA/mm^2 [see Fig. 3(b)] under the magnetic field. Because the magnetic field direction is perpendicular to the corrosion current direction, the observation of a sudden increase followed by a slow decrease in the current density is attributed to the combined action of the Lorentz and gradient forces of the magnetic field. This indicates that the main difference in the corrosion current density curve profiles for B//E and B⊥E originates from the action of the Lorentz force because the Lorentz force is small for B//E, and that for B⊥E is almost negligible. Figs. 3(a) and 3(b) confirm that the current density decreased (increased) due to the gradient force (Lorentz force) of the magnetic field for B//E and B⊥E because the lower value of the corrosion current density (black double-headed arrows) is approximately 0.1 mA/mm^2 for both cases after the application of the magnetic field.

In addition, we observed that the corrosion current density of carbon steel for B⊥E suddenly increased after the application of the magnetic field and then slowly decreased, which is attributed to the competition between the Lorentz force and the gradient force of the magnetic field. Here, the Lorentz force increases the current density by enhancing the mass-transport processes [30]. The gradient force decreases the current density by suppressing the convection of solution through the adsorption effect of the gradient force on the iron ions (Fe^{2+} and Fe^{3+}) to the anode, which increases the concentration of corrosion products on the carbon steel surface [31].

After removing the NdFeB magnet, we observed that the final value of the current density is lower than the initial value for B//E and B⊥E (e.g., approximately 2.11 mA/mm^2 for B//E and approximately 2.04 mA/mm^2 for B⊥E). This means that magnetic field potentially affects the formation of an intermediate on the surface of carbon steel, according to the following reactions [32]:

$$\begin{cases} Fe \rightarrow Fe^{2+} + 2e^- \\ Fe^{2+} \rightarrow Fe^{3+} + e^- \\ Fe^{3+} + 3OH^- \rightarrow FeOOH + H_2O \end{cases} \tag{1}$$

To confirm the formation of intermediate on the surface of carbon steel, the composition of the intermediate product on the surface of carbon steel was analysed using X-ray diffraction (XRD) after the experiments for B//E (B⊥S) and B⊥E (B//S). As expected, Figs. 3(c) and (d) show that the intermediate product is mainly composed of NaCl and FeOOH. NaCl originates from seawater (cubic symbols), and FeOOH is the intermediate product on the surface of carbon steel (red lines). However, Figs. 3 (a) and 3 (b) show that the final current density for B⊥E is lower than that for B//E after removing the magnetic field; this observation occurs due to the combined action of the enhancing effect of the Lorentz force on the mass-transport processes [30] and the adsorption effect of the gradient force on the iron ions (Fe^{2+} and Fe^{3+}) towards the anode, which considerably accelerates the formation of intermediate products for B⊥E. As explained in Ref. [31], the Lorentz force drives convection, and the magnetic gradient force allows paramagnetic ions to adsorb on the surface of carbon steel. The combination of both forces results in the formation of more intermediate products on the surface of carbon steel for B⊥E.

3.4. Effect of the Lorentz force on potentiodynamic polarization

To verify the effect of Lorenz force on the electrochemical corrosion behaviour of carbon steel for B//E and B⊥E, a uniform magnetic field was considered. By changing the uniform magnetic field strength and direction, the potentiodynamic polarization behaviour was investigated, as shown in Figs. 4(a) and 4(b). Through experimentation and by comparing the slopes of the plots for the cathode and anode, we determined that the anode reaction on carbon steel is dominant [19]. To quantitatively compare the results for B//E and B⊥E, the electrochemical corrosion potential was calculated from the potentiodynamic polarization curves by Tafel extrapolation. For B//E, the electrochemical corrosion potential (U_E) does not exhibit a clear trend with increase in the magnetic field strength from 0 mT to 40 mT, as shown in Fig. 4(c) (solid black line). For B⊥E, the electrochemical corrosion potential shifts to the negative value (towards the anode) with the increase in the magnetic field strength, as shown in Fig. 4(c) (solid red line). This suggests that the Lorentz force accelerates the corrosion rate of carbon steel through the effect of the uniform magnetic field on the mass transport process.

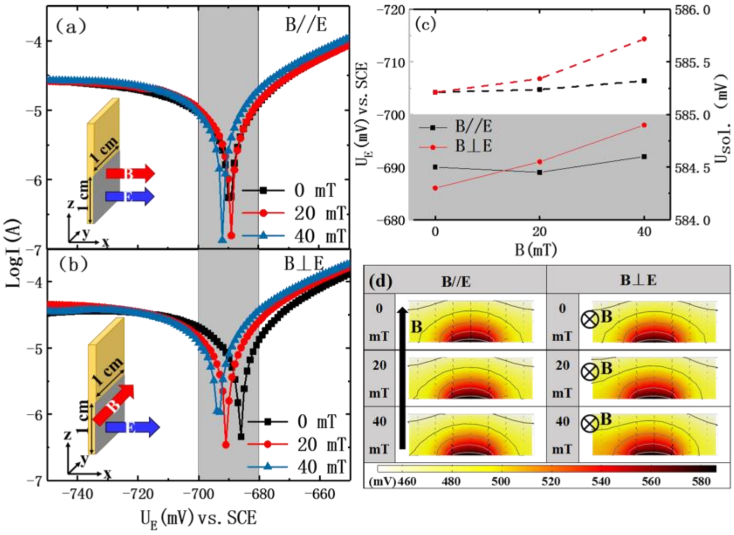

Figure 4. Potentiodynamic polarization curves for 0, 20, and 40 mT magnetic field for (a) B//E and (b) B⊥E. (c) Comparison of the experimental U_E and numerically simulated U_{sol} for B//E and B⊥E. (d) Numerical simulation results on the effects of the magnetic field strength and layout on the electrolyte potential distribution

To analyse the effect of the magnetic field on the mass transfer process in the electrochemical corrosion reaction of carbon steel, the electrical potential distribution around carbon steel was examined for B//E and B⊥E by the finite element electrochemical simulation [33]. Because local salinity (local free ion concentration) in the real ocean does not considerably change, the second current distribution model of the electrochemical corrosion is considered to simulate the conductivity of the electrolyte and the kinetics of the electrode reaction.

In this model, there is only one modelling domain [i.e., the electrolyte domain close to the anode electrode (carbon steel electrode)] as shown in Fig. 4(d). Carbon steel is a high electrical conductor and is not included in the model. Therefore, only the effective reaction surface of carbon steel is set to be the anode electrode. The boundary condition at the electrode that is directly opposite of the anode is set as the cathode, as follows:

$$n \cdot i_l = \sum_m i_{loc,m} \tag{2}$$

where, $i_{loc,m}$ is the reaction current density of the cathode electrode. Insulation is another boundary condition.

In this model, only the effect of magnetic field on the electrolyte potential is evaluated during the process of Fe oxidation in carbon steel by considering the reduction and transfer of oxygen, because seawater is a weakly basic solution, as follows [32]:

$$\textbf{Anode: } Fe \rightarrow Fe^{2+} + 2e^-, \tag{3}$$

$$\textbf{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^-. \tag{4}$$

Here, the equilibrium potentials of the electrode reaction are $U_{eq} = -0.76V$ (for Fe) and $U_{eq} = 1.229V$ (for O_2). The secondary current distribution interface is used to solve the electrolyte potential, as follows:

$$i_l = -\sigma_l \nabla \phi_l \tag{5}$$

$$\nabla \cdot i_l = 0 \tag{6}$$

Here, i_l is the electrolyte current density vector, σ_l is the electrolyte conductivity, and ϕ_l is the electrolyte potential.

Fig. 4 (d) shows the effect of magnetic fields on the electrolyte potential (U_{sol}) with potential nephograms near the anode electrode for B//E and B⊥E. With increase in the magnetic field strength, we observed that for B⊥E, the change in the electrolyte potential is more significant than that for B//E; this suggests that the effect of the Lorentz force on the transmission of the electrolyte carrier (OH^-) near the cathode for B⊥E is larger than that for B//E [31]. The electrolyte potential trend is consistent with the experimental results [dotted red line in Fig. 4(c)]; this means that the diffusion and convection behaviour of OH^- in the seawater can be accelerated by the Lorentz force to enhance the oxygen reduction of the cathode [32]. Therefore, the corrosion reaction of carbon steel in the anode is more accelerated by the Lorentz force for B⊥E compare with that for B//E (Fig. 3).

4. CONCLUSION

The effect of magnetic field on the corrosion behaviour of carbon steel in static seawater was studied using electrochemical corrosion experiments and finite element electrochemical simulations. We determined that the magnetic gradient and Lorentz forces affect the corrosion process of carbon steel because carbon steel is a magnetic material. In the presence of the magnetic field, we confirmed the acceleration action of the Lorentz force and the inhabitation action of the gradient force on the corrosion of carbon steel. These results are important for the anti-corrosion research in seawater.

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