Shift of the Iron Corrosion Potential and Acceleration of the Mass Transport of Dissolved Oxygen by the Micro-MHD Effect

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Change in the corrosion rate of iron under a high magnetic field was examined by determining corrosion potential shifts and polarization curve measurements. With increasing magnetic flux density, the electrode potential shifted to the anodic side. This was induced by a cathodic diffusion current increment via a microscopic stirring effect in the local magnetohydrodynamic flow, which arose from interaction between the electrochemical corrosion current and the applied magnetic field.

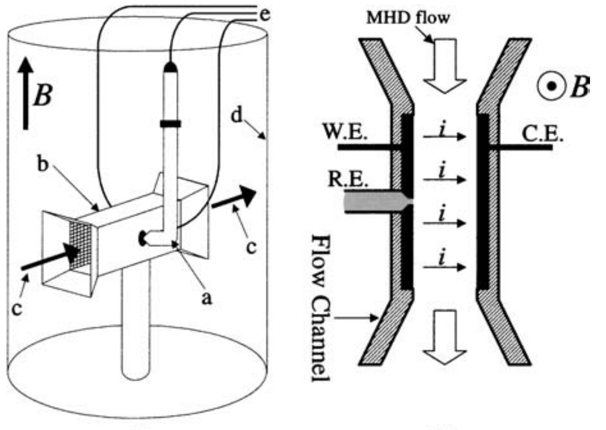
Iron has historically been one of the most technologically important industrial materials. It has found application within even the most difficult environments, including under high magnetic fields. Increasing application of iron in superconducting technologies, including plasma confinement, accelerators such as cyclotrons, energy storage coils, and non-energy-loss power transmission has led to strong interest in phenomenon that arise from the properties of iron under high magnetic fields.

From electrochemical models of metal corrosion, it is known that local electrochemical circular currents within the corrosion reaction can interact with an external magnetic field and induce local magnetohydrodynamic (MHD) flow.[1,2] The so-called micro-MHD effect, by its microscopic stirring action, leads to enhancement in the rate of iron-oxygen corrosion, which is rate limited by the mass transport of dissolved oxygen.

In this paper, we examine iron corrosion through analysis of the electrode potential and polarization curve measurements.

In Figure 1, a schematic illustration of the electrochemical cell is shown. The MHD electrode (MHDE), which was designed to measure the MHD flow effect on the electrochemical process, was utilized.[3] The MHDE was composed of a rectangular channel (2.4 cm in length, 1 cm in height, 5 mm in width, made of acrylic resin) with two open ends. Inside the channel, a pair of iron electrodes ($1 \times 2\,\mathrm{cm}^2$ in area, 99.7% in purity) were embedded in a face-to-face orientation on the inner walls. A magnetic field was vertically applied to the electric current flowing between the electrodes. The Lorentz force, which is generated along the channel, moves the solution from one open end to the other in the channel. The electrode potential was regulated using a reference electrode (BAS, Ag/AgCl electrode RE-1B) connected to the backside of the working electrode through the Luggin capillary.

The MHDE cell was dipped in a vessel filled with a $0.5\,\mathrm{mol\,dm^{-3}}$ sodium chloride solution, which was saturated with dissolved oxygen under atmospheric conditions. The solution pH was 7.0, thus neutral, and the temperature was controlled at 300 K by circulating water jacket. The vessel was then placed in the center of a magnetic field that was generated by a liquid helium-less superconducting magnet (Sumitomo Heavy Industries Ltd., model HF10-100VHT-1). The electrodes were connected to the outer electric circuits using a shielded cable. The corrosion potential was then measured using an electrometer. For polarization curve measurements, the electrode potential was controlled by a potentiostat (TOHO GIKEN Ltd., PS-2000).



(i) (ii)

Figure 1. Schematic illustration of the MHD electrode. (i) Appearance. a; Luggin capillary connected to Ag/AgCl reference electrode, b; flow channel made of acrylic resin, c; MHD flow, d; vessel, e; read line to the potentiostat. (ii) Cross section of the MHD electrode.

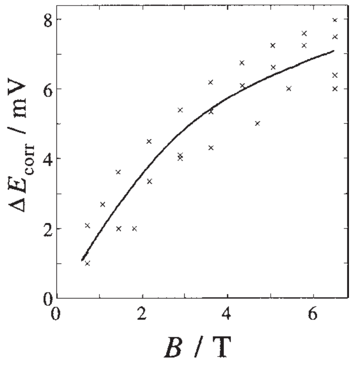


Figure 2. Iron corrosion potential shift plot for the applied magnetic flux density. Solution contain; $0.5\,\mathrm{mol\,dm^{-3}}$ NaCl and saturated with air, T; 300 K.

Figure 2 plots the relationship between the corrosion potential shift ΔE_{corr} and the applied magnetic flux density. In this plot, ΔE_{corr} shifts to the anode side with increasing magnetic flux density.

Figure 3 is the polarization curve of the iron-MHDE. The anodic branch was unchanged although the cathodic diffusion

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limited current was enhanced by application of an 8 T applied magnetic flux density. In Fig. 3, i_{0T}, i_{8T}, and E_{0T}, E_{8T} are the corrosion currents and corrosion potentials obtained by extrapolation of linear region in the polarization curves. The order of the corrosion potential shift from polarization measurement $\Delta E_{corr} = 10\,mV$ shows good agreement with that from potential different measurement in Fig. 2.

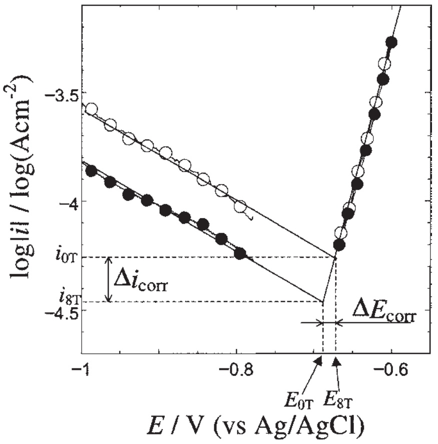

Figure 3. Polarization curves for iron MHDE in 0.5 mol dm^{-3} sodium chloride solution. ●; 0 T, ○; 8 T. i_{0T}, i_{8T}; corrosion current under 0 T and 8 T, E_{0T}, E_{8T}; corrosion potential. Solid lines show the extrapolation of linear region of the each current branch.

Under the current conditions with high concentrations of sodium chloride, iron corrosion is not observed as localized pitting, but as uniform corrosion because of the passive film break induced by the absorbed chloride ion.[4] In an electrochemical local cell model, such iron corrosion has the attack of dissolved oxygen formally summarized as;

(i) anodic reaction

$$Fe + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 3e \tag{1}$$

(ii) cathodic reaction

$$3/4O_2 + 3H^+ + 3e \rightarrow 3/2H_2O \tag{2}$$

(iii) total reaction

$$Fe + 3/4O_2 + 3/2H_2O \rightarrow Fe(OH)_3 \tag{3}$$

Each anodic and cathodic reaction occurred independently, yet to maintain the conservation of electrical quantities, they must be balanced. Therefore, the current at the anode and cathode must be equal. In the present case, the anodic dissolution rate of iron was determined using only the electrode potential. This reaction is rate determined by the thermodynamic potential gap between the electrode and solution. From an energetic viewpoint, the magnetic field is considered to play no role in the physicochemical process, because of the very small perturbation induced for chemical species. Even under magnetic fields up to 10 T, the Zeeman energy increment of an electron is less than 0.1% of the potential energy in the normal chemical reaction.[1]

Yet for the cathodic branch, which is limited by the mass transport of dissolved oxygen, the reaction rate will be enhanced with increasing fluid flow at the electrode surface.[3]

As another possibility for the driving force of the magnetic field effect on mass transport, the magnetic force, which is induced by the special gradient of the magnetic energy, is considerable one.[1] In the present case, magnetization of the iron electrode may induce a strong gradient in the magnetic field near the electrode surface. In this arrangement, the electrode surface facing parallel to the applied magnetic flux, the magnetic flux density near the electrode will be reduced. This is the result of an overlap of the counter magnetic field induced by the magnetization of iron. When only the cathodic reaction is considered, consumption of dissolved oxygen may lead to a decrease in the magnetic susceptibility of the test solution per unit volume. The anodic reaction, in contrast, exhibits increased magnetic susceptibility of the solution upon production of iron hydroxide. From calculation of the magnetization per unit mass in the reaction formula of equation 3, magnetic susceptibility of the test solution will be decreased with progression of the entire reaction.[1] Therefore, the spatial geometry of the magnetic susceptibility gradient of the solution and the magnetic field gradient is stable at the reaction interface. A negligible magneto-convection effect, which occurs from magnetization forces, is expected. Mass transport enhancement of the cathodic branch in the polarization curve may be a result of the effect induced only by the Lorentz force.

When considering that the log of the anodic current is proportional to over potential and that current balance must be maintained between the anodic and cathodic reactions, the corrosion potential shifts in proportion to the log of the increase in the cathodic current. In this scheme, we can estimate variation in the iron corrosion rate Δi_{corr} from the corrosion potential shift ΔE_{corr} directly. And in present case, ΔE_{corr} shows the acceleration of Δi_{corr} by magnetic field that was applied parallel to the electrode surface, thus, iron corrosion rate increased with applied magnetic flux density.

By utilizing electrochemical corrosion potential measurements and polarization measurements, an acceleration of the iron corrosion in sodium chloride solution by the magnetic field was demonstrated. This enhancement was a result of acceleration in mass transport brought about by stirring from the micro-MHD effect. These results show that corrosion potential shift is connected to the corrosion rate change directly in diffusion controlled metal corrosion system. It is suggested that results from the micro-MHD system for nonferromagnetic materials can be utilized on ferromagnetic materials in this special case, i.e., the effect of magnetization was negligible. The results in this examination will be the bridgehead from which a study of ferromagnetic material surface properties in a high magnetic field environment will be approached.

References

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