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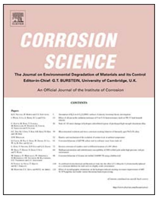

A magnetic field induced undulated surface and the shift of the active/passivation transition threshold of iron in a sulfuric acid solution

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ABSTRACT

An unevenly distributed magnetic field caused irreversible electrochemical states of iron in a sulfuric acid solution due to the undulated surface generated by anodic dissolution. The magnetic field affected the activation-passivation transition threshold by modifying the interface reaction rate and surface morphology. The passivation onset potential was increased by decreasing the scan rate under 0.4 T, and was insensitive to the scan rate at 0 T.

1. Introduction

Anodic dissolution and passivation of iron in sulfuric acid solutions is a classic and widely studied system in the fields of corrosion science and engineering [1–15]. The effects of applied magnetic fields on the behavior of anodic polarization, including the periodic current oscillation of iron in sulfuric solutions, have been investigated via potentiodynamic and potentiostatic polarization measurements or by other observation and monitoring techniques [16–30]. The shifts of the characteristic potentials and current densities of the anodic polarization curves have been attributed to the Lorentz-force-driven magnetohydrodynamics (MHD) effect [31–38], Kelvin-force-driven magnetic field gradient force (MFGF) effect [38–49] or both. Jiang et al. [48] have investigated the enhancing effect of a weak magnetic field on the removal of Cu^{2+} ions by zero valent iron. They pointed out that the magnetic field could accelerate the adsorption of paramagnetic Cu^{2+} on the surface of zero valent iron, resulting in the galvanic corrosion of zero valent iron through MFGF. The magnetic fields could also enhance the corrosion of zero iron and the removal of Cu^{2+} by MHD effect. Li et al. [49] have found that the MFGF by weak magnetic field was a major driving force for the enhanced effect on the removal of Cr^{6+}, and the magnetic field effect was more significant when the particle size of zero valent iron was smaller.

Macroscopically uneven anodic dissolution of iron in sulfuric acid solutions has been observed in the presence of magnetic fields [16,18,25], and has been attributed to the uneven distribution of the induced magnetic field on the iron electrode surface as well as the MFGF [18,25]. It has been postulated that the undulated electrode surface evolved from the magnetic field effect would simultaneously affect the dissolving/passivating transition, which needs to be clarified in detail. In the present work, electrochemical measurements of iron in sulfuric acid with switching of the magnetic field on/off are used to investigate the effect of magnetic field on the anodic behavior and threshold condition for the active dissolution to passivation transition as the results of the magnetic field effects on the reaction rates and electrode surface morphology.

2. Material and methods

Industrial iron of 99.5% purity was used. The experimental setup is schematically shown in Fig. 1. Instead of using an H-shaped electrochemical cell, as in previous experiments [16–18], the electrochemical cell used in the present work was a 160 mm × 20 mm × 100 mm rectangular chamber. In the previous work [18], the effect of magnetic field from 0.15 T to 0.4 T on the anodic dissolution of iron in sulfuric acid solutions were studied, and the severely local dissolution at two edge areas of the iron electrode was found under a 0.4 T magnetic field. In this work, we focused on the undulated surfaces induced by anodic dissolution for various polarization periods under 0.4 T magnetic field and their further effect on the active/passivation transition threshold of iron in a sulfuric acid solution. A magnetic field of 0.4 T (T) was generated using an electromagnet with an EM-3 type DC galvanostatic

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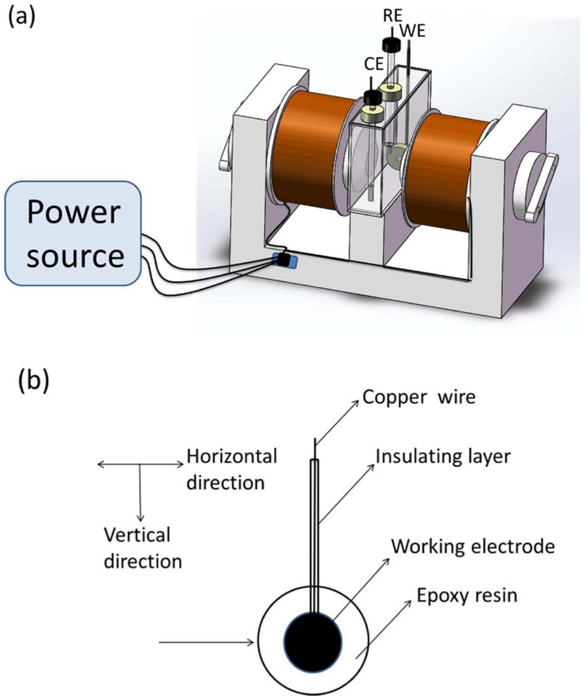

Fig. 1. Schematic of the electrochemical cell a) and the electrode for measurements under magnetic fields b).

power source. The magnetic field was imposed on the working electrode of the electrochemical cell. The working electrode surface was placed vertically. The direction of the magnetic field was horizontal and was parallel to the surface of the working electrode. Potentiodynamic polarization curves and potentiostatic polarization measurements were conducted with a CORST CS-310 electrochemical workstation. The pure iron working electrode was 5 mm in diameter, with an exposed surface area of approximately 0.2 cm^2, and was sealed in an epoxy resin insulator. The electrode surface was polished to a 1500 grit finish and then rinsed in ethanol and acetone in sequence prior to the electrochemical tests. The counter electrode consisted of platinum plates and the reference electrode was a saturated calomel electrode (SCE). A tube with a ceramic junction was used as the interface between the reference electrode and test solution to avoid contamination of the solution from the reference electrode. All of the potentials were measured and quoted against SCE. The test solution was a naturally aerated 1.0 mol/L H_2SO_4 solution prepared with analytical grade reagents and deionized water. All of the electrochemical measurements were performed at room temperature, approximately 25 °C. The electrode surfaces after the anodic polarization measurements were observed with a VHX-100 type optical microscope and a HITACHI SU-1500 type scanning electron microscope.

3. Results

3.1. Potentiodynamic anodic polarization curves with and without a 0.4 T magnetic field

Potentiodynamic anodic polarization curves measured at potential scan rates from 0.167 mV/s to 5.0 mV/s of iron in a 1.0 mol/L H_2SO_4 solution under a 0 T or 0.4 T magnetic fields are shown in Fig. 2. All of the polarization curves showed typical active-passive characteristics. The anodic polarization behaviors of iron in acid solutions under 0 T have been widely investigated and analyzed [1–15] and the shapes of anodic polarization curves have been discussed in detail by Keddam [11]. The presence of $i_{max,1}$ was due to the temporary coverage of the electrode with a slightly soluble species (prepassive film) which acted as an inhibitor on the active dissolution, and $i_{max,2}$ corresponded to the threshold condition for the formation of stable passive film, resulting in two peaks under 0T. Magnetic field increased the dissolution rate of the prepassive film thus eliminated the first current peak in the anodic polarization curves.

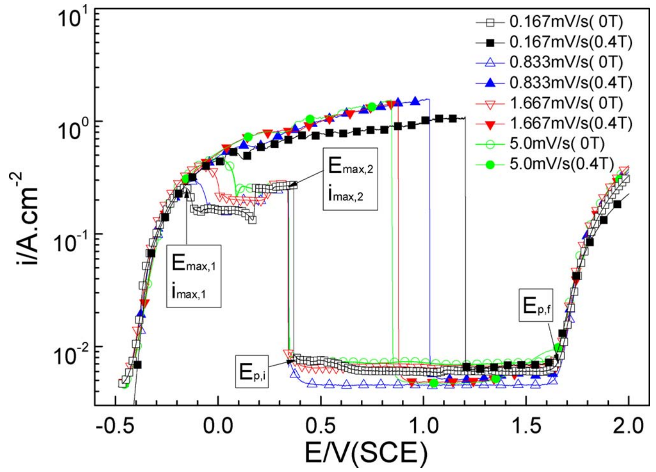

Fig. 2. Anodic polarization curves for iron in a 1.0 mol L^{-1} H_2SO_4 solution under a 0 T and 0.4 T magnetic fields at potential sweep rates of 0.167, 0.833, 1.667 and 5.0 mV/s.

Under 0 T, increasing the potential scan rate increased the first peak current density $i_{max,1}$ and first peak potential $E_{max,1}$, but did not significantly affect the second peak current density $i_{max,2}$, second peak potential $E_{max,2}$, passive region starting potential $E_{p,i}$ (called the passivation onset potential in this work), passive region ending potential $E_{p,f}$ or width of the passive region. Under the 0.4 T magnetic field, increasing the potential scan $E_{max,2}$ rate over the range of 0.167 mV/s to 5.0 mV/s decreased $E_{max,2}$. $i_{max,2}$ in the presence of the 0.4 T magnetic field was insensitive to the potential scan rate over the range of 0.833 mV/s to 5.0 mV/s, which was significantly higher than that was obtained at 0.167 mV/s.

The applied magnetic field did not have any significant effect on the current density in the initial active dissolution range, but increased the current density in the pre-passive range as well as the threshold potential and current density for the onset of passivity in the polarization curve, which is consistent with previously reported observations [16–25]. The potential scan rate and magnetic field did not have any significant effect on the current density at potentials higher than $E_{p,f}$, where the reaction is mainly oxygen gas evolution. The current density in the passive region was not strongly affected by the applied magnetic field.

3.2. Potentiostatically anodic polarization under 0 T and 0.4 T magnetic fields

Potentiostatic polarization measurements were used to determine the anodic dissolution behaviors at various potentials as well as the threshold conditions for the onset of passivation under 0 T and 0.4 T magnetic fields. Current density vs. time (i-t) curves for iron in 1.0 mol/L H_2SO_4 at various anodic potentials, as shown in Fig. 3a–t. The electrode was in the active dissolution state in the presence and absence of the 0.4 T magnetic field at 0.20 V (SCE) with an anodic current density of ~0.25 A/m^2 at 0 T and ~0.81 A/m^2 at 0.4 T, showing an increase of the anodic current density of approximately 0.56 A/m^2 after imposing the 0.4 T magnetic field and vice versa after withdrawing the 0.4 T magnetic field, as shown in Fig. 3a and b. If the electrode was initially polarized at 0.28 V (SCE) at 0 T, high amplitude current oscillations occurred (Fig. 3c), and the electrode state was shifted to an active dissolution state after imposing a 0.4 T magnetic field, while the electrode state could not return to the current oscillation state after