

## **A study of the effect of magnetic fields on the diffusion layer at the Fe/H<sub>2</sub>SO<sub>4</sub> interface by holographic microphotography**

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The effect of externally imposed magnetic fields on the relaxation of the concentration diffusion layer at the Fe/0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> interface after passivation of the iron electrode during potentiodynamic polarization was studied by holographic microphotography. The presence of a magnetic field was found to retard the relaxation process while the microturbulence was impeded.

*Keywords:* diffusion layer, relaxation process, magnetic field, holographic microphotography, microturbulence.

### INTRODUCTION

As a new branch of electrochemistry, magneto-electrochemistry has drawn a lot of attention in the last two decades, not only because electrochemical processes under magnetic fields promise great potential in application, but also because magneto-electrochemistry manifests significant theoretical implications as a interdisciplinary area of investigation.<sup>1,2</sup> Visualization techniques, such as interferometry<sup>3–5</sup> and analytical indicator means,<sup>6,7</sup> are effective for the examination of the effects of magnetic fields on the flow patterns adjacent to the electrode surface. By holographic microphotography, the anodic dissolution and potentiostatic current oscillations of iron, and reactivation of passivated iron in sulfuric acid solutions in a weak magnetic field have been studied.<sup>8–10</sup> The externally imposed magnetic field has been found to accelerate mass transport by magnetohydrodynamic flow, which affects the dissolution of iron in the prepassive region and changes the current oscillatory behaviour. The present paper focuses on the effect of the magnetic field on the relaxation of the diffusion layer at the Fe/0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> interface in a specified period, namely, after passivation of the iron electrode during potentiodynamic polarization. This study may yield some insight into the corrosion process of iron in an externally applied magnetic field.

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## EXPERIMENTAL

The working electrode, 2 mm in diameter, was prepared from an iron rod of 99.99 % purity (JMC 848 specpure, Johnson Matthey Chemicals). The electrode was carefully sealed with epoxy resin in a glass tube, leaving only the working surface exposed to the solutions. Before each experiment, the specimen was mechanically polished with emery papers to a mirror-like brightness, and cleaned with alcohol and then triply distilled water in an ultrasonic bath.

The electrolyte,  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution, was prepared from analytical grade reagent and triply distilled water. A large sheet of platinum was used as the counter electrode. Potentials were measured with respect to a  $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  reference electrode and converted to the standard hydrogen electrode (NHE). All measurements were performed at  $15 \pm 1 \text{ }^\circ\text{C}$ .

By means of a PAR M173 potentiostat and a PAR M175 function generator, the electrode potential was swept from the corrosion potential,  $E_{\text{corr}}$ , to the desired potential,  $+1.180 \text{ V}$ , at  $10 \text{ mV s}^{-1}$ , both in the absence and presence of a magnetic field. The polarization curves were obtained on a Houston Instrument 2000  $X$ - $Y$ - $t$  recorder. The dynamic change of the iron/solution interface during the above electrode process was videotaped synchronically. The holograms presented in this paper were transferred from the video tape with the help of a computer.

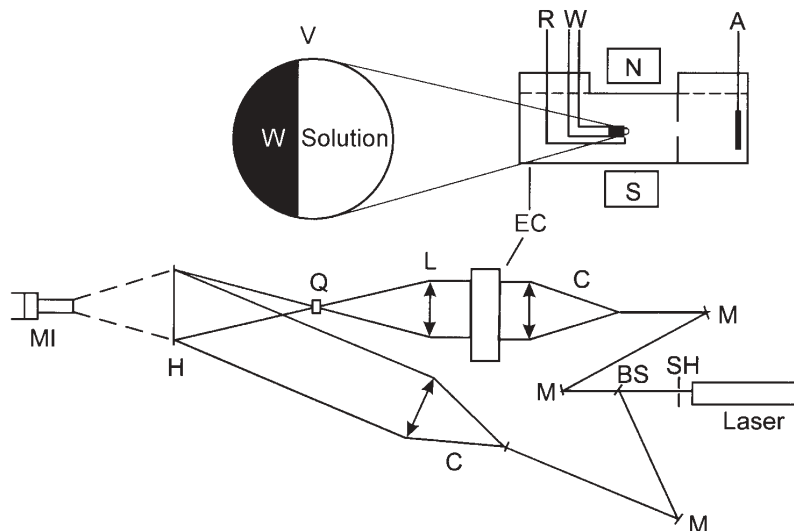


Fig. 1. Schematic diagram of the arrangement for holographic microphotography, and configuration of the magnetic field and the electrochemical cell. SH – shutter; BS – beam splitter; M – mirror; C – collimator; L – imaging lens; Q – phase filter; H – holographic plate; MI – microscope; EC – electrochemical cell; W – iron electrode; R – reference electrode; A – counter electrode; N, S poles of the permanent magnet, V – view observed through holographic microphotography.

The holographic light path, and the configuration of the magnetic field and the iron electrode are illustrated in Fig. 1. For the convenience of the holographic microphotography, a small permanent magnet was used. The orientation of the magnetic field was vertical since a horizontal magnetic field could block the light path. The density of the applied magnetic flux could be measured by a Gaussmeter *via* a Hall probe. The cell was centered carefully between two  $314 \text{ mm}^2$  magnet poles prior to the experiment. The degree of non-uniformity of the magnetic field in the experimental area was not more than 1 % at a magnetic flux density of 60 mT. The electrochemical cell had three chambers. An aperture of 12 mm in diameter was left between the working and the counter electrode chambers in order to minimize possible solution movements caused by hydrogen evolution on the platinum electrode.

The details of the procedures for the holographic microphotography can be found in a previous publication,<sup>11</sup> and, therefore, will not be detailed here.

### RESULTS AND DISCUSSION

The potentiodynamic polarization curves of the iron electrode in  $0.5 \text{ mol dm}^{-3}$

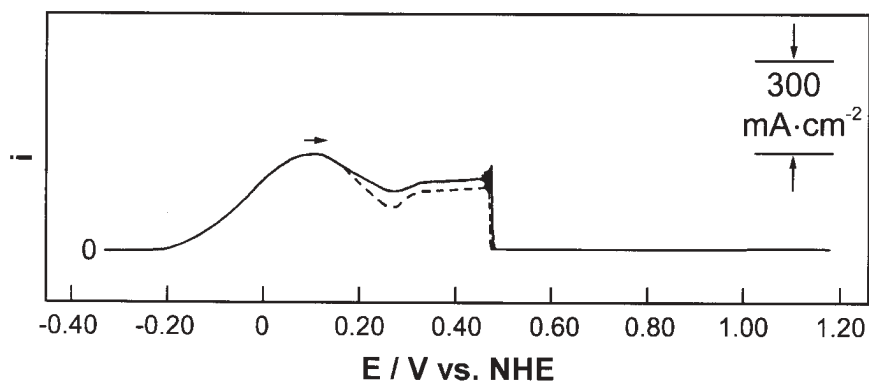


Fig. 2. Potentiodynamic polarization curves of the iron electrode in  $0.5 \text{ mol cm}^{-3} \text{ H}_2\text{SO}_4$  solutions at  $10 \text{ mV s}^{-1}$  with or without the application of an external magnetic field: (---)  $B = 0 \text{ mT}$ , (—)  $B = 60 \text{ mT}$ .

$\text{H}_2\text{SO}_4$  solutions in the presence and absence of a magnetic field are shown in Fig. 2. If the transpassive range is neglected, the overall anodic process of iron dissolution can be roughly

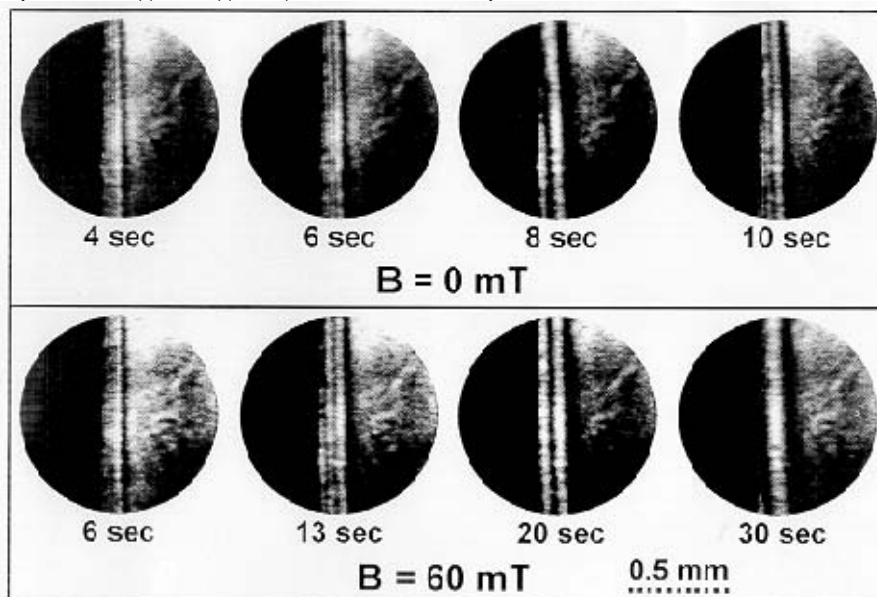
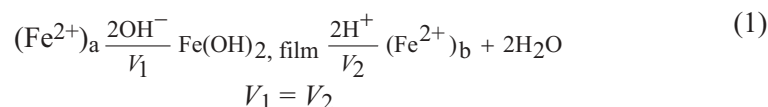


Fig. 3. Holograms of the iron/solution interface obtained at selected time instants when the concentration diffusion layer is dispersing following the passivation of the iron electrode in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  solution, with or without the application of the external magnetic field.

divided into the active range, the prepassive range and the passive range. When the electrode potential is anodically swept to 470 mV, *i.e.*, when the iron electrode moves from the prepassive region to the passive region, the thick prepassivation film suddenly disappears, and an obvious diffusion layer emerges in its place.<sup>11</sup> The holograms in Fig. 3, taken at selected time instants after the sudden drop of the current density and the simultaneous shift of the electrode into the passive region, show the gradual fading of the diffusion layer at the electrode/electrolyte interface in the presence or absence of the magnetic field. The number of fringes at the interface indicates the degree of the concentration gradient. The number decreases together with the concentration gradient.

On the basis of the holographic dynamic observation of the microchanges at the iron/solution interface and the XPS analysis of the film formed on the electrode surface,<sup>11</sup> it is found that the dissolution of iron in the prepassive range is mainly dependent on the dynamic equilibrium of the formation and dissolution of the Fe(OH)<sub>2</sub> thick film<sup>8</sup>



Here, (Fe<sup>2+</sup>)<sub>a</sub> refers to Fe<sup>2+</sup> ions in the vicinity of the electrode; (Fe<sup>2+</sup>)<sub>b</sub>, to Fe<sup>2+</sup> ions in the bulk of the electrolyte. When the potential of the iron electrode is swept to the Flade potential, an extremely thin, yet compact bilayer with Fe<sub>3</sub>O<sub>4</sub> inside and γ-Fe<sub>2</sub>O<sub>3</sub> outside is formed on the electrode surface, which leads to a sharp decrease of the current, which in turn stops more Fe(OH)<sub>2</sub> from being formed, *i.e.*, V<sub>1</sub> = 0. Thus the equilibrium of formation and dissolution of Fe(OH)<sub>2</sub> is disturbed, leading to the swift dissolution of Fe(OH)<sub>2</sub>, due to its unstable nature in acidic medium. Therefore, the thick film disappears and the obvious diffusion layer emerges in its place.<sup>11</sup> Then, the gradual decrease of the interference fringes in the holograms indicates that the concentration diffusion layer slowly shrinks until it disappears completely. Compared with the case in the absence of the magnetic field, the relaxation of the diffusion layer in the presence of a magnetic field is noticeably slowed down.

While studying the effect of the magnetic field on the electrolysis of Cu | CuSO<sub>4</sub> | Cu and Zn | ZnSO<sub>4</sub> | Zn systems, O'Brien *et al.* observed similar behavior when the electrolysis was terminated.<sup>4,5</sup> They believed that this was due to the fact that the microturbulence had been inhibited or that the viscosity of the solution had been changed in the presence of the magnetic field.

The present study differs from that of O'Brien *et al.* in at least two aspects. Firstly, an electric field was imposed in our experiments in addition to the magnetic field. In other words, the electrolysis was still under process. In the light of the structure of the passive film, it can be concluded that the electric field mainly falls on the passive film, while the potential drop on the solution phase is very small. Therefore, the existence of the electric field does affect the process, though in a mild way. Moreover, the majority of the ions in the solution are not paramagnetic Cu<sup>2+</sup> or diamagnetic Zn<sup>2+</sup> ions, but ferromagnetic Fe<sup>2+</sup> whose existence is the key factor in the suppression of the relaxation process. With a magnetic field present, in the vicinity of the iron solution interface, the

higher the concentration  $\text{Fe}^{2+}$  becomes, the smaller the magnetic resistance and the lower the energy will be. However, as the concentration diffusion layer relaxes, the magnetic resistance goes up and so does the energy level. As a result, the relaxation of the concentration diffusion layer is obviously inhibited in a magnetic field. In other words, microturbulence is impeded under the influence of an external magnetic field. In addition, after passivation of the iron electrode, the electric field continues to exist but the current density is almost reduced to zero. Although the relaxation of the concentration gradient is primarily the result of diffusion and electrical migration with natural convection, the movement of the charged particles in a magnetic field is impeded to some extent, thus the relaxation time is lengthened.

It should be stated that the changes in the concentration gradient is not only related to concentration differences, but also determined by the orientation of the magnetic field, the electric field, and the gravitation field. In a word, it is a complicated phenomenon, which calls for further study.

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## ИЗВОД

ПРОУЧАВАЊЕ УТИЦАЈА МАГНЕТНОГ ПОЉА НА ДИФУЗИОНИ СЛОЈ НА ГРАНИЦИ  $\text{Fe}/\text{H}_2\text{SO}_4$  ПОМОЋУ ХОЛОГРАФСКЕ МИКРОФОТОГРАФИЈЕCHAO WANG<sup>1,3</sup> и SHENHAO CHEN<sup>2,3</sup>

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Холографском микрофотографском техником проучаван је утицај споља наметнутог магнетног поља на концентрациони дифузиони слој на површини Fe електроде у  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  током потенциодинамичке поларизације. Нађено је да магнетно поље успорава релаксациони процес после наметнуте микротурбуленције.

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