Effect of Magnetic Fields on the Behavior of Iron Electrodeposition

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The behavior of iron deposition in a horizontal magnetic field was studied by electrochemical analysis. The influences of cathodic polarization curve, cyclic voltammetry, potentiostatic polarization and electrochemical impedance on the process of iron electrodeposition under magnetic field in different directions to current were investigated. The results showed that the mass transport process and charge transfer process were enhanced by applying magnetic fields.

Keywords: Electrodeposition; Magenetic field; Iron; Electrochemical analysis; MHD effect

1. INTRODUCTION

Since the 1970s, researchers have tried to apply magnetic field in the process of electrodeposition, and found a series of unique phenomena in the process of deposition, which has attracted great attention of many researchers around the world and has been rapidly developed. It is a comprehensive new technology across the fields of electromagnetics, electrochemistry and materials science, and gradually developing into a new interdisciplinary zones, namely, magneto-electrochemistry[1-2]. With the application of strong magnetic field of superconductors in the 1990s, electrochemical research under strong magnetic fields has been developing rapidly and become widespread concerned[3-5].

The electrodeposition reaction on the cathode surface consists of ion transfer, electrochemical reaction and new phase formation. Magneto-electrochemistry technology mainly uses the composite action of Lorentz force generated by the interaction between magnetic field and electrolytic current induces a convection flow called magnetohydrodynamic (MHD) flow, magnetization force, and magnetic Gibbs free energy on the dispersion, stability, bath property, electrode particle mass transfer
process, ion movement, electrochemical reaction, coating surface state and metal atom nucleation, crystallization, growth and grain orientation, which can improve the structure, morphology and properties of the coating[6-8]. The morphology of electrodeposits is especially sensitive to magnetic fields when the Lorentz force interferes with natural convection[9]. In recent years, the external electromagnetic field has attracted more and more attention of researchers due to its advantages of easy control, high energy density, non-contact energy transfer, non pollution and high selectivity for the prepared materials[10].

According to our previous research work[11-14], the application of magnetic field has a significant effect on Fe-Si composite electrodeposition. When a parallel magnetic field was applied, with the increase of magnetic field strength, the "needle-like" protrusion on the surface of the coating gradually become a "dome" structure. When perpendicular magnetic field was applied, the "stripe-like" protrusion appeared on the coating surface. It is generally known that there is no unified theory for electroplating under magnetic field at present, which is mainly attributed to the influence of MHD effect induced by the interaction of magnetic field and current on the electrodeposition process. In this paper, the influence of magnetic field on the discharge process of Fe	extsuperscript{2+} is analyzed by discussing the polarization curve, cyclic voltammetry, potentiostatic polarization and electrochemical impedance of the cathode. At the same time, due to the serious reaction of hydrogen evolution, this work only studies the effect of pure iron electrodeposition under a horizontal magnetic field with different direction arrangement to current.

2. EXPERIMENTAL

The basic electroplating solution used in this experiment consists of FeCl	extsubscript{2}-4H	extsubscript{2}O (30g/L), FeSO	extsubscript{4}-7H	extsubscript{2}O (250g/L) and NH	extsubscript{4}·Cl (50g/L). All reagents are analytical pure. In this work, CHI 660C electrochemical workstation (Chenhua, CHI, China) and a typical three-electrode glasses cell were used for electrochemical experiments (40×40×70mm), which can hold 100ml of plating solution. Two electrodes are installed in the center of the corresponding cell walls. The distance between the electrodes is 40 mm, and the reference electrode is fixed in the center of the cell. The circular glassy carbon electrode was used as the working electrode (4 mm in diameter), the circular platinum plate as the counter electrode (15 mm in diameter), and the saturated calomel electrode (SCE) as the reference electrode. Before electrochemical test, the pH value was adjusted to 1.5 by dilute sulphuric acid. The polarization curve, cyclic voltammetry, potentiostatic polarization and electrochemical impedance measurements were used to investigate the effect of magnetic field on the iron deposition process. The potential of cyclic voltammetry curve is -1.15V(vs. SCE) and the scanning rate is 10 mV/s. The linear polarization curve is from open circuit potential to -1.2V(vs. SCE) with the scanning rate of 1 mV/s. All potentials are relative to saturated calomel electrode potentials. The impedance bias potential is from -0.8V to -1.15V(vs. SCE), and the frequency is from 100kHz to 0.01Hz with the amplitude of 5 mV.

So far, the electrochemical study of iron deposition in magnetic field is very few. In Bund’s research[15], it was thought that natural convection plays a very important role in electroplating process under a magnetic field. When without mechanical stirring, the direction of natural convection is vertical upward. Therefore, the influence of Lorentz force and natural convection on the deposition process must
be considered when analyzing the influence of horizontal magnetic field on the behavior of iron electrocrystallization. Therefore, the relationship between magnetic field and current is considered in this paper. The relationship between the magnetic field and the electric field is different every 90° when the vertical placed electrodes rotates horizontally, after the magnetic field direction is the same as the current direction (Figure 1(a)), which is called a parallel magnetic field. When the direction of magnetic field is opposite to that of electric field, it is called anti-parallel magnetic field(Figure 1(b)). Theoretically, there is no Lorenz force when the magnetic field and current are parallel or antiparallel, but it can be ascertained the micro MHD effect exists from our previous experiments[11-14]. When the current and magnetic field are perpendicular to each other, the direction of Lorentz force generated is vertical upward (Fig. 1(c)), which is called perpendicular magnetic field. Similarly, when the direction of Lorentz force generated is vertical downward, it is called anti-perpendicular magnetic field(Fig. 1(d)).

Figure 1. Diagram of the direction relationship between applied magnetic field and current, parallel magnetic field(a), anti-parallel magnetic field(b), perpendicular magnetic field(c) and anti-perpendicular magnetic field(d)

3. EXPERIMENT RESULTS

3.1 Effect of magnetic field on polarization curve

Figure 2 shows the influence of the magnetic field on the polarization curve. It can be seen that the discharge potential of Fe$^{2+}$ is about -0.96V(vs. SCE) without magnetic field. After applying a magnetic field, the electrodeposition potential under a magnetic field obviously moves forward regardless of the arrangement of the magnetic field and the current direction. Moreover, with the increase of the magnetic field intensity, the discharge potential of Fe$^{2+}$ becomes more positive. The experimental results are similar to result of Hu et al.[16], it is believed that this effect is mainly caused by MHD effect. The effect of MHD on mass transfer can be expressed by limiting current in electrochemical reaction[17-19]. Fahidy[20] found that the limiting current density increased significantly with the increase of magnetic field intensity(B).

$$j_L = j^0_L + aB^m$$

(1)

Where $j_L$ and $j^0_L$ denote the limiting current density without magnetic field and with a magnetic field respectively, a and M are empirical constant. It is generally believed that $j_L$ is proportional to $B^{1/3}$[21-23]. The thickness of cathode dispersion layer can be expressed by the following equation:

$$\delta = \delta_0 - a_2B^{m_2}$$

(2)

Where $\delta_0$ and $\delta$ represent the thickness of the dispersion layer without and with magnetic field.
respectively, and $a_2$ and $m_2$ are constants. With the increase of magnetic field intensity, the thickness of dispersion layer will be reduced.

Figure 2. Effect of magnetic field intensity on polarization curve for a parallel magnetic field(a), perpendicular magnetic field(b), anti-parallel magnetic field(c), anti-perpendicular magnetic field(d). $[\text{FeCl}_2\cdot4\text{H}_2\text{O}]=0.15\text{M}$; $[\text{FeSO}_4\cdot7\text{H}_2\text{O}]=0.90\text{M}$; $[\text{NH}_4\cdot\text{Cl}]=0.93\text{M}$; pH=1.5 and T=25°C.

Figure 3. Schematic diagram of ions migration during electrodeposition without magnetic field(a) and with a magnetic field(b)

In the process of $\text{Fe}^{2+}$ discharge, $\text{Fe}^{2+}$ is consumed continuously on the cathode surface with the
reaction process, which leads to the deficiency of $\text{Fe}^{2+}$. When the magnetic field is applied, the MHD effect caused by the interaction of magnetic field and current promotes the transfer of $\text{Fe}^{2+}$ to the cathode surface, thus reducing or even eliminating the concentration polarization near the cathode surface (Figure 3).

According to formula of Lorenz force ($f_L$):

$$ f_L = B \times J_p, \quad (3) $$

where $J_p$ is a current component perpendicular to direction of the magnetic field ($B$). When under a perpendicular magnetic field, the Lorentz force theoretically reaches maximum and which can even reach the strength of mechanical agitation in high magnetic field [24]. A strong scouring effect on the electrode surface will be formed (Figure 4a). After applying a parallel magnetic field, there is no Lorentz force in theory. However, the electrode is not ideal smooth, and with the process of electrodeposition, the electrode surface becomes uneven, resulting in the current and magnetic field is not parallel from microcosmic angle, there exists a current component perpendicular to the magnetic field (Figure 4b-c) [25-28]. As a result, a micro MHD effect near the electrode surface is induced and promotes the mass transfer of the solution. At the same time, Zhou et al [29-31] found that the parallel magnetic field can even lead to the macro MHD effect when under a strong enough magnetic field. However, under the same intensity of magnetic field, the macro MHD effect caused by a perpendicular magnetic field should be significantly stronger than that caused by a parallel magnetic field with the same intensity. Therefore, the effect of perpendicular magnetic field on the discharge potential of polarization curve should be more positive.

![Figure 4. Schematic diagram of MHD effect during electrodeposition under a magnetic field (a) in a perpendicular magnetic field (b-d) under a parallel magnetic field](image)
In order to clarify the effect of the relationship between magnetic field and electric field on deposition current, Figure 5 shows the influence of magnetic field direction with different field intensity on deposition current. It can be seen that in the magnetic field of 0.1~1 T, in general, the general trend is that the polarization current is the larger under the condition of anti-perpendicular magnetic field and anti-parallel magnetic field, than that of under a parallel or perpendicular magnetic field. On the one hand, a greater intensity of convective mass transfer induced by the MHD effect in perpendicular magnetic field than that in a parallel magnetic field, resulting in a larger Faraday current in the polarization curve. On the other hand, Fe$^{2+}$ is paramagnetic and magnetic field gradient force may plays an important role in the electrodeposition process[29, 32].

![Figure 5](image-url)

**Figure 5.** Effect of magnetic field direction on polarization curve under different magnetic field intensity (a) 0.1T; (b) 0.5T; (c) 0.7T; (d) 1T. [FeCl$_2$$\cdot$4H$_2$O]=0.15M; [FeSO$_4$$\cdot$7H$_2$O]=0.90M; [NH$_4$Cl]=0.93M; pH=1.5 and T=25°C.

### 3.2 Effect of magnetic field on cyclic voltammetric curve

Figure 6 shows the effect of magnetic field intensity on cyclic voltammetric curves under different conditions. From the Figure 6, it can be seen that there is a current peak between 0.2V and 0.4V(vs. SCE), which indicates that the discharge reaction or intermediate product is formed at this potential. The peak current at the potential in the absence of magnetic field is significantly higher than that of with a magnetic field. With the increase of magnetic field intensity, the peak current shows a linear downward trend. At the same time, there is an oxidation peak between -0.5V and -0.3V(vs. SCE). It shows that the crystallization process of Fe$^{2+}$ in the electrodeposition system has gone through the
nucleation stage, and a continuous coating has been formed at the cathode. The peak current of oxidation peak also decreased with the application of magnetic field in different directions.

Figure 6. Effect of magnetic field on cyclic voltammetry curve under a parallel magnetic field (a), perpendicular magnetic field (b), anti-parallel magnetic field (c), anti-perpendicular magnetic field (d). [FeCl$_2$·4H$_2$O]=0.15M; [FeSO$_4$·7H$_2$O]=0.90M; [NH$_4$·Cl]=0.93M; pH=1.5 and T=25°C.

Above analysis shows that the discharge reaction of Fe$^{2+}$ or hydrogen evolution reaction cannot occur at the potential of 0.2V~0.4V(vs. SCE), it may be caused by the presence of flocculent iron oxides. Fe$^{2+}$ exists stably at a lower pH value in the early stage of electrodeposition. With the progress of discharge reaction, the concentration of H$^+$ decreases due to the side reaction of hydrogen evolution reaction, and the flocculent oxides of Fe(OH)$_3$ and Fe(OH)$_2$ may easily form, which in turn promotes the formation of oxidation. After the magnetic field is applied, the MHD effect promotes the mass transfer near the cathode surface, complements H$^+$ and makes the pH value not rise excessively, thus inhibits the formation of these series of oxides. As a result, the cyclic voltammetric curve shows a decreased peak current with the increase of the magnetic field.

Matsushima et al.[33-34] found that the application of magnetic field significantly reduced the current efficiency of cathode iron, which is consistent with our previous experimental results[13], so it will affect the crystallization process of the coating. The application of magnetic field reduced the thickness of the coating, which may be exhibited in the decrease of the oxidation peak of -0.5V ~ -0.3V(vs. SCE). However, Figure 6 also shows that the difference of influence on peak current is not obvious under different types of magnetic field, this may be contributed to the combined action of
concentration gradient force, magnetic field gradient force, MHD effect, natural convection and other factors[29, 32].

3.3 Influence of magnetic field on potentiostatic polarization curve

In order to clarify the effect of magnetic field on the limiting current in iron electrodeposition, Figure 7 shows potentiostatic polarization tests curve at a constant applied voltage of -0.95V~1.2V(vs. SCE) without magnetic field. From Figure 7, the nucleation and growth process of iron electric crystallization process can be obtained. Above the potential of -1.0V(vs. SCE), the current drops rapidly at the initial stage, and then reaches a steady state. At this potential, the system only undergoes Faraday process such as double layer charging or the reaction ion transforms into intermediate product without nucleation and precipitation, which is consistent with the previous results of polarization curve and cyclic voltammetry.

When the potential is lower than -1.0V(vs. SCE), the current increases with time and then tends to be stable, which indicates that the process of electrocrystallization occurs. However, there is no peak current at the potential of -0.95V~ -1.2V(vs. SCE). First, the electrode surface is not an ideal crystal surface, and there are steps, dislocations and other defects. Therefore, the reduced metal ions can grow directly at the defects without going through the nucleation stage. At this time, the current curve can not detect the appearance of the peak current. Second, the crystallization process may also be three dimensional nucleation growth model with overlapping growth centers.

![Figure 7.](image)

Figure 7. potentiostatic polarization tests under different potential(vs. SCE) without magnetic field. [FeCl₂·4H₂O]=0.15M; [FeSO₄·7H₂O]=0.90M; [NH₄·Cl]=0.93M; pH=1.5 and T=25°C.

Figure8 and Figure 9 show the effect of magnetic field intensity on the chronoamperometry curve under different types of magnetic fields. The chronoamperometry curves are all measured at the cathode potential of -1.15V(vs. SCE). At this potential, each current curve begins to rise and then tends to be stable. However, compared to the curve obtained without magnetic field, both the parallel and perpendicular magnetic fields can increase the limiting current of the electrodeposition process. Similar trend results are also existed in anti-parallel and anti-perpendicular magnetic fields. Therefore, it can be inferred the nucleation and growth mode of iron does not change after the application of magnetic field,
but a micro MHD effect or macro MHD effect induced by the interaction of magnetic field and current increase the mass transfer of electroplating solution, thus promoting the discharge process of iron and hydrogen ions. At the same time, it is found that the potentiostatic polarization curve are not smooth at the potential of -1.2V(vs. SCE) without magnetic field and at -1.15V(vs. SCE) under an 1T magnetic field, which may be caused by the disturbance of cathode surface state and nearby solution caused by the aggravation of hydrogen evolution process. In our previous work[12-13], it has discussed that the application of magnetic field could reduce the current efficiency and aggravate the side reaction of hydrogen evolution reaction. The above results of potentiostatic polarization confirm that the magnetic field enhanced the mass transport progress.

![Figure 8. Potentiostatic polarization behaviors of iron coatings at the cathodic potential of -1.15V vs. SCE under parallel magnetic field.][1] [FeCl₂·4H₂O]=0.15M; [FeSO₄·7H₂O]=0.90M; [NH₄·Cl]=0.93M; pH=1.5 and T=25°C.

![Figure 9. Potentiostatic polarization behaviors of iron coatings at the cathodic potential of -1.15V vs. SCE under perpendicular magnetic field.][2] [FeCl₂·4H₂O]=0.15M; [FeSO₄·7H₂O]=0.90M; [NH₄·Cl]=0.93M; pH=1.5 and T=25°C.

### 3.4 Influence of magnetic field on electrochemical impedance spectroscopy

Figure 10 shows the Nyquist curve of the electrochemical impedance spectrum of iron deposition.
at different potentials. It can be seen from the above results of cyclic voltammetry and polarization curve that the reduction process of Fe$^{2+}$ ion in electroplating solution starts at -1.0 V (vs. SCE). Therefore, the appearance of inductive arc in Nyquist curve indicates that the electrode is covered by iron deposition layer. The formation of iron coating can also be observed on the cathode surface after the test. When the effect of glassy carbon electrode on the potential is not considered, the deposition potential of Fe$^{2+}$ is calculated theoretically, approximately -0.682V (vs. SCE) and that for H$^+$ is -0.3325V (vs. SCE). Therefore, it can be considered that at a high potential, Hydrogen(H$_2$) formed by the discharge of H$^+$, which disturbing the surface state of the electrode, so the Nyquist curve obtained is not smooth. At the same time, due to the progress of electrodeposition, flocculent oxides such as Fe(OH)$_2$ and Fe(OH)$_3$ may be produced on the electrode surface, which will make the Nyquist curve more fluctuating.

Figure 11 shows the effect of magnetic field intensity on Nyquist curve of iron electrodeposition at -1.15V (vs. SCE). It can be seen from the that, regardless of the relative position of magnetic field and electric field, the diameter of capacitive arc of electrodeposition system after applying magnetic field is smaller than that without magnetic field. With the increase of magnetic field intensity, the diameter of capacitive arc becomes smaller.

Figure 10. Nyquist curve of electrochemical impedance spectrum at different polarization potentials without magnetic field. [FeCl$_2$·4H$_2$O]=0.15M; [FeSO$_4$·7H$_2$O]=0.90M; [NH$_4$Cl]=0.93M; pH=1.5 and T=25°C.
Figure 11. Effect of magnetic field intensity on electrochemical impedance spectrum at the cathodic potential of -1.15 V (vs. SCE) for parallel magnetic field (a), perpendicular magnetic field (b), anti-parallel magnetic field (c), anti-perpendicular magnetic field (d). [FeCl₂·4H₂O]=0.15M; [FeSO₄·7H₂O]=0.90M; [NH₄·Cl]=0.93M; pH=1.5 and T=25℃.

Figure 12. Equivalent circuit diagram of electrodeposition system

This shows that the application of magnetic field reduces the impedance of electrodeposition system. This trend is similar to the research results of Wang et al. [35-36]. Most of the present results show that MHD effect promotes the mass transfer of electroplating solution [37-39], and decrease resistance of the reduction reaction of Fe²⁺ ion in solution.

The equivalent circuit diagram (C(R(CR))) was shown in Figure 12. In the diagram, C_d represents the double electric layer capacitance of the electrode, R_f is the solution resistance, R_r is the reaction resistance and C_r is the double electric layer capacitance. Then the measured impedance spectrum is fitted. Table 1 shows the equivalent circuit fitting parameters of electrodeposition impedance under different magnetic fields. After applying magnetic field, compared with the test results without magnetic field, the solution resistance and reaction resistance showed a significant downward trend, the reaction resistance showed a gradually decreasing trend with magnetic direction of parallel→anti-parallel→anti-parallel→perpendicular, while the solution resistance showed a decreasing trend of anti-parallel→parallel→anti-perpendicular→perpendicular, that is to say, related reduction for perpendicular magnetic field was more significant than that of the parallel magnetic field. It shows that the MHD effect induced by the interaction of magnetic field and current plays a very important role, and indicates the macro MHD effect induced by the perpendicular magnetic field is stronger than the micro MHD effect induced by parallel magnetic field, which greatly promotes the mass transfer of electroplating solution, reduces the solution resistance near the cathode surface and accelerated discharge process. At the same time, the MHD effect promotes the transfer behavior of Fe²⁺ in solution to the cathode surface and
reduces the reaction potential of Fe$^{2+}$, so it will reduce the resistance of electron transfer during the discharge of Fe$^{2+}$.

| Table 1. Impedance fitting parameters of iron electrodeposition in different systems |
|------------------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| B (T) | Ca/10$^8$F | Cr/10$^8$F | Rf/Ω | Cr/10$^8$F | Rf/Ω | Cr/10$^8$F | Rf/Ω | Cr/10$^8$F | Rf/Ω |
|       |            |               |      |            |       |            |       |            |       |
| 0.0T  | 4.07       | 19.29         | 30.04| 15.55      | 4.07  | 19.29      | 30.04| 15.55      | 4.07  |
| 0.1T  | 3.59       | 18.87         | 9.20 | 14.51      | 4.06  | 18.46      | 13.07| 13.99      | 38.39 |
| 0.3T  | 4.29       | 18.60         | 14.08| 14.66      | 6.41  | 18.45      | 15.04| 12.34      | 43.32 |
| 0.5T  | 3.36       | 18.79         | 8.80 | 12.75      | 5.51  | 18.40      | 15.19| 12.52      | 39.76 |
| 0.7T  | 3.16       | 18.57         | 7.72 | 12.81      | 6.07  | 18.43      | 16.49| 11.53      | 37.43 |
| 1.0T  | 3.85       | 18.56         | 11.35| 12.60      | 5.61  | 18.18      | 17.82| 9.20       | 39.16 |

4. CONCLUSIONS

The influence of magnetic field on the electrodeposition crystallization process of pure iron was studied by electrochemical analysis. It is found that the MHD effect by the interaction between the magnetic field and the current has a significant effect on the electrodeposition of iron. The following conclusions obtained are as follows:

- The analysis of polarization curve shows that Fe$^{2+}$ starts to discharge and reduce at about -0.97V(vs. SCE) without magnetic field. After applying magnetic field, the limit current of cathode increases significantly, and makes the discharge potential of Fe$^{2+}$ move forward obviously.

- The results of cyclic voltammetry show that there is a reduction current peak between 0.2 V and 0.4 V(vs. SCE), and an oxidation peak between -0.5V and -0.3V(vs. SCE). With the increase of magnetic field intensity, the peak current decreased significantly.

- Simultaneously, the results of the potentiostatic polarization indicates that the limit current is increased whether the perpendicular magnetic field or the parallel magnetic field is applied.

- Analysis of electrochemical impedance shows that the solution resistance near the cathode and the electron transfer resistance of Fe$^{2+}$ discharge are reduced after applying a magnetic field.

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