A Kinetic Study on the Fe–Zn–P Coatings by Electrodeposition

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A kinetic study on the electrodeposition of Fe–Zn–P ternary alloys onto steel in chloride solutions was carried out using a rotating disc geometry. Mass transfer through diffusion layer controlled the deposition rates of zinc onto steel, and those of iron and phosphorus were controlled by the rates of both electrochemical reaction and mass transfer. The zinc content in the Fe–Zn–P alloy increased with stirring speed and voltage. However, iron content in the Fe–Zn–P alloy decreased with speed and voltage. The phosphorus content is almost constant with respect to stirring speed in the lower voltage range but decreased slightly with stirring speed in the higher voltage range.

1. Introduction

It has been known that electrodeposited Fe–Zn alloy coatings can provide steel better corrosion protection, weldability and paintability than electro-galvanized coatings.[1] The zinc-iron alloy deposit containing about 5 to 10 mass% of iron was developed by Japan.[2,3] An anomalous codeposition phenomena was observed for the zinc-iron system and the reduction of ferric to ferrous ions in the bath was also studied by Lee.[4] Fe–Zn–P ternary coatings to steel were recently developed by Kawasaki steel Co. in Japan.[5] They reported that the paintability and adhesion to substrate was excellent when 0.1 to 0.5 mass% of phosphorus was maintained in the coating. However, detailed technical know how has not been open. A Fe–Zn–P ternary coating has a good paint adhesion so that reduce the two-step coatings, namely, phosphating and Zn–Fe coatings to one-step. In this study, kinetics and mechanism of Fe–Zn–P coatings in chloride solutions has been investigated using a rotating disc electrode.

2. Theoretical Background

Electrodeposition reaction can be described as heterogeneous in nature, and the overall reaction consists of a number of sequential steps such as convective diffusion, electromigrations and electrochemical reaction at solution/metal interface.

The equation for the convective mass transfer to a rotating disc under laminar flow conditions was originally given by Levich[6]

$$J_L = -(V/A)(dC_{b,i}/dt) = 0.62D^{2/3}v^{-1/6}\omega^{1/2}C_{b,i} = k_L C_{b,i} \tag{1}$$

where J_L: convective mass flux (mole/cm²·s), V: volume of solution (cm³), A: surface area of rotating disc (cm³), k_L: mass transfer coefficient by convective diffusion (cm/s) ($= 0.62D^{2/3}v^{-1/6}\omega^{1/2}$), D: diffusivity of the depositing metallic ion (cm²/s), v: kinematics' viscosity of the solution (cm²/s),

ω: angular velocity of the rotating disc (s⁻¹), $C_{b,i}$: bulk concentration of the depositing ions (moles/cm³).

The equation for the electromigration[7] of depositing ions can be described as

$$J_E = Z_i\mu_i F C_i \nabla\phi \tag{2}$$

where J_E: ion flux (mol/cm⁻²·s), Z_i: charge on species i (equiv/mol), μ_i: mobility (cm²·mol/J·s), F: Faraday's constant (96487 C/equiv.), $\nabla\phi$: potential gradient (V/cm). Therefore, total mass transfer coefficient for the convective diffusion can be described by the sum of mass transfer and electromigration

$$k_T = k_L + k_E = 0.62D^{2/3}v^{-1/6}\omega^{1/2} + Z_i\mu_i F C_i \nabla\phi \tag{3}$$

where, k_T is total mass transfer coefficient, k_L is mass transfer coefficient for the convective diffusion and k_E is electromigration coefficient. Apparent mass flux obtained can be written by

$$J_i = (-1/A)(dm_i/dt) = (-V/A)(dC_b/dt)$$
$$= k_T \cdot (C_{b,i} - C_{s,i}) \tag{4}$$

where m_i is number of moles of i species, V is volume of electrolyte (cm³), A is geometrical area of cathode (cm²) and $C_{s,i}$ is surface concentration of depositing i species (mol/cm³).

The rate of electrodeposition at the cathode surface was given by Butler-Volmer.[8]

$$v_i = -dC_{s,i}/dt = A/V \cdot k_c \cdot C_{s,i}^n = A/V \cdot k_e^{-\beta n_i \eta \Phi/PT} C_{s,i}^n \tag{5}$$

where k_c ($= k_e^{-\beta n_i \eta \Phi/PT}$) and k_e are rate constants for chemical reaction and for electrochemical reaction, respectively, β is a symmetry factor, n_i is number of electrons involved in the deposition reaction, η is overvoltage and n is order of reaction. At steady state, the rate of electrodeposition reaction equals the mass transfer rate:

$$k_c \cdot C_{s,i}^n = k_T \cdot (C_{b,i} - C_{s,i}) \tag{6}$$

Table 1   Chemical composition of substrate steel plate.

C	Mn	P	Al	S	Ti	N	O	Fe
0.002%	0.12%	0.012%	0.040%	0.10%	0.039%	13 ppm	36 ppm	Bal.

Table 2   Standard chemical composition of Fe–Zn–P bath.

Compound	Composition (kg/m^3)
FeCl·6H$_2$O	198.7
ZnCl$_2$	13.6
NaPH$_2$O$_2$·H$_2$O	21.4
NH$_4$Cl	20
Na$_3$Cit	30
KCl	100

Table 3   Standard experimental condition of Fe–Zn–P electrodepositon.

Experimental term	Standard condition
Stirring speed (r.p.m.)	400
Temperature (K)	313
Voltage (vs. SCE)	1.41
Fe ion concentration of bath (M)	0.9
Zn ion concentration of bath (M)	0.2
Phosphorus concentration of bath (M)	0.21

For a first-order chemical reaction, with $n = 1$

$$C_{s,i}^n = C_{b,i} \cdot k_T/(k_c + k_T) \tag{7}$$

And substituting (7) into (5) results

$$-dC_{b,i}/dt = A/V[(k_c \cdot k_T)/k_c + k_T]C_{b,i} \tag{8}$$

3.   Experimental

Electrodeposition experiments were carried out batchwise in a $5 \cdot 10^2$ cm^3 glass vessel using a 3.00 cm diameter disc of steel plate (Table 1), which was coated with 4.00 cm diameter of teflon.[8] Insoluble graphite plate was used as anode and saturated calomel electrode as non-polarizable reference electrode. All electrolytes (Table 2) were prepared by dissolving analytical grade reagents in distilled water. The pH of the electrolyte was controlled by NH4OH and measured by pH meter (Fisher Accumet model 620). The voltage was controlled by D.C. power supply (HP-6642A, Hewlett Packard).

The rate of electrodeposition was calculated by the weight differences before and after deposition experiment and the alloy composition was determined by EPMA [JXA-8600SX (JEOL)] analysis.

The standard experimental conditions are shown in Table 3.

4.   Results and Discussions

4.1   Effect of metal contents of bath

The variations of iron and zinc contents in the Fe–Zn–P alloy with the bath composition were shown in Fig. 1. The iron content in the Fe–Zn–P alloy was less than 15 mass% until the molar ratio of iron to zinc in the bath reached to 4.5
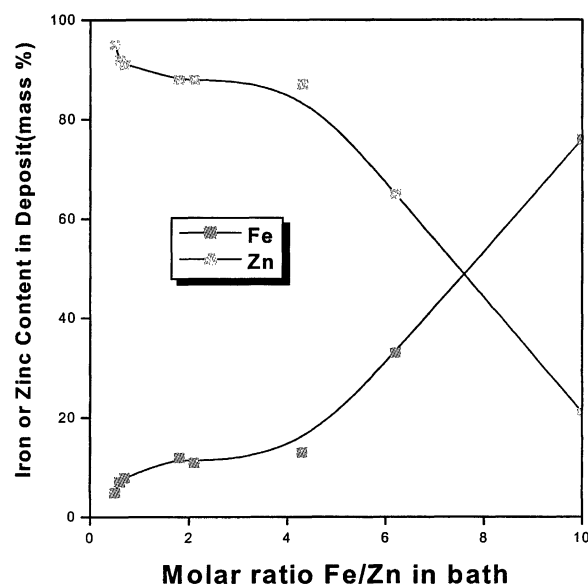

Fig. 1   Relation between the molar ratio of metallic ion of the bath and the composition of electrodeposited Fe–Zn–P alloys at -1.4 V. (vs. SCE). 400 r.p.m., and 40°C.

and it increased 80 mass% when the molar ratio of iron to zinc in the bath reached to 10. This anomalous codeposition[9] was shown in the Fe–Zn–P ternary alloy system. The optimum iron content for the automobile body in the Fe–Zn–P alloy is believed to be 15–20 mass%.[10] From experimental results and above-mentioned report, the molar ratio of iron to zinc should be maintained at 4.5 to get optimum iron content in the coatings.

4.2   Effects of stirring speed and voltage

The effects of stirring speed and voltage on the deposition rate of iron, zinc and phosphorus were studied and the results are shown in Figs. 2 to Fig. 7. The plots of the rate constant against the square root of stirring speed show straight-line relationships and the rate constant of iron was slightly increased with the increase of ω 1/2 (Fig. 2). However, it can be seen from Fig. 3 that effects of stirring speed and voltage on the deposition rate of zinc were much more pronounced than those of iron. The slope of k vs. ω 1/2 increases with voltage. This phenomenon was also observed in the Zn–Fe system by Tripathi and Udupa.[11] The rate constant of phosphorus was almost constant with the variation of stirring speed and voltage (Fig. 4).

Tafel plots for these elements are shown in Figs. 5–7 and the results showed that plots of logarithm of rate constant against cathode potential of iron and zinc did not give straight-line relationship (Figs. 5 and 6) but the plot for phosphorous showed straight-line (Fig. 7). From the previous results of Figs. 2 to 6, the rates of iron and zinc deposition were thought to be controlled by both electrochemical reaction and mass transfer. However, the rate of phosphorus deposition was
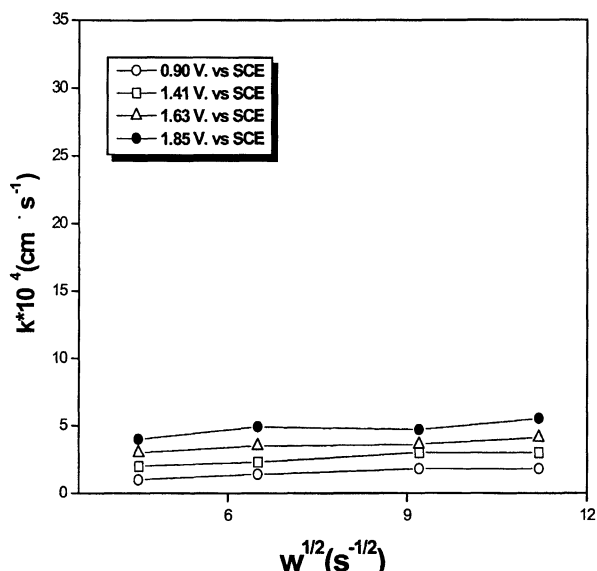
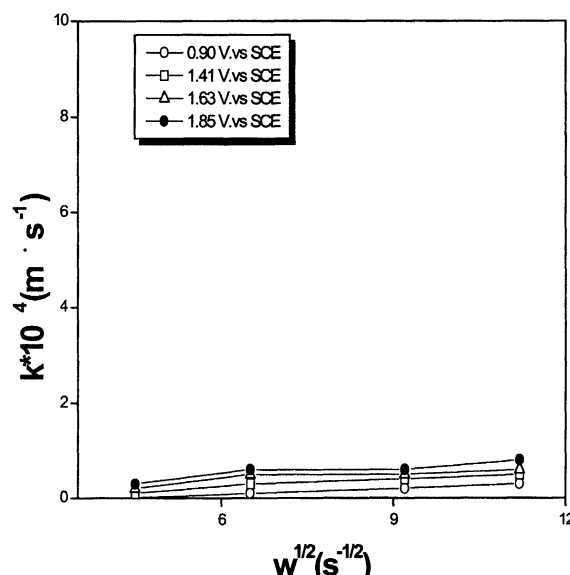Fig. 2   The effect of cathode potential on the deposition rate constant of Fe at 313 K.

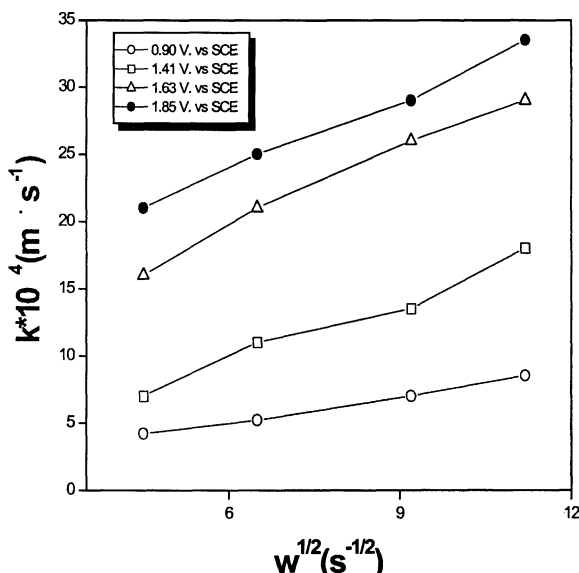Fig. 4   The effect of cathode potential on the deposition rate constant of P at 313 K.

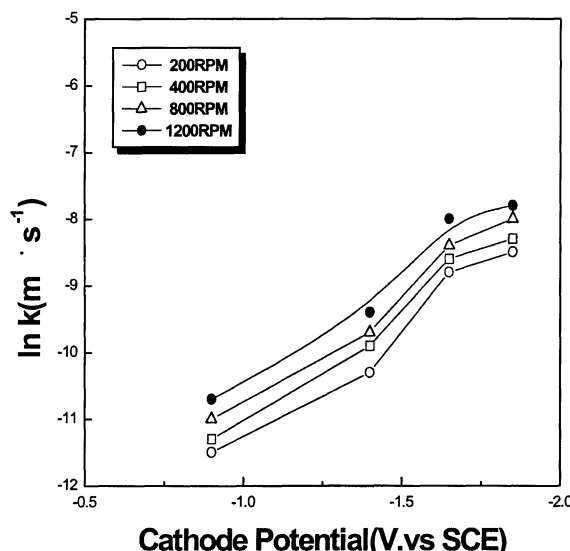Fig. 3   The effect of cathode potential on the deposition rate constant of Zn at 313 K.

Fig. 5   The effect of rotating speed on the deposition rate constant of Fe at 313 K.

thought to be controlled by electrochemical reaction at the cathode surface.

The effects of stirring speed and voltage on the metal content in Fe–Zn–P alloys were investigated and the results are shown in Figs. 8 to 10. The iron content in the alloy decreased with angular velocity and the negative effect of angular velocity on the amount of iron content was pronounced with voltage. For example, the iron content in the alloy decreased from 10 to 5 mass% when stirring speed increased from 200 (ω = 20.79) to 1200 (ω = 125.66) r.p.m. at −0.90 V (vs. SCE) and decreased from 40 to 32 mass% at −1.85 V (vs. SCE).

The zinc content increased with the increase of stirring speed (Fig. 9). For example, the zinc content in the deposit increased approximately by 5 mass% at −0.90 V (vs. SCE) and by 10 mass% at −1.85 V (vs. SCE). The phosphorus content was almost constant with the increase of ω 1/2 in the lower

voltage ranges from −0.9 to −1.41 V (vs. SCE). However, it decreased slightly with the increase of ω 1/2 at 1.85 V (vs. SCE) (Fig. 10). The effect of angular velocity on the amount of phosphorous content is similar with that of iron content, indicating that the mechanism of phosphorus deposition is the same as that of iron.[12]

4.3   Effect of temperature

The temperature dependence of electrodeposition reaction of Fe–Zn–P system was studied and Arrhenius plots are shown in Fig. 11. Apparent activation energies for zinc, iron and phosphorus were 5.1, 13.2 and 20.5 kcal/mole, respectively. From the activation energy thus obtained, the deposition rate of zinc is thought to be controlled by both electrochemical reaction and mass transfer, which proceeds under "mixed control".[13] However, the deposition rates of phosphorous are thought to be controlled by electrochemical reaction.
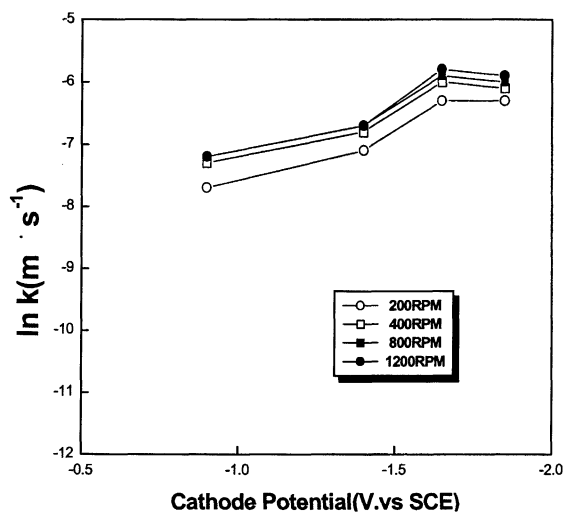
Fig. 6 The effect of rotating speed on the deposition rate constant of Zn at 313 K.
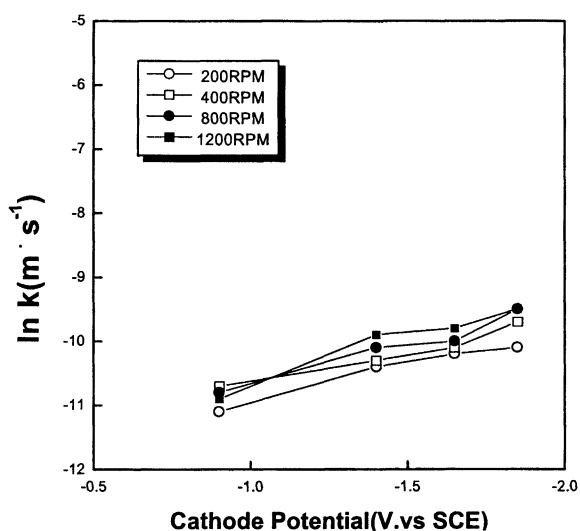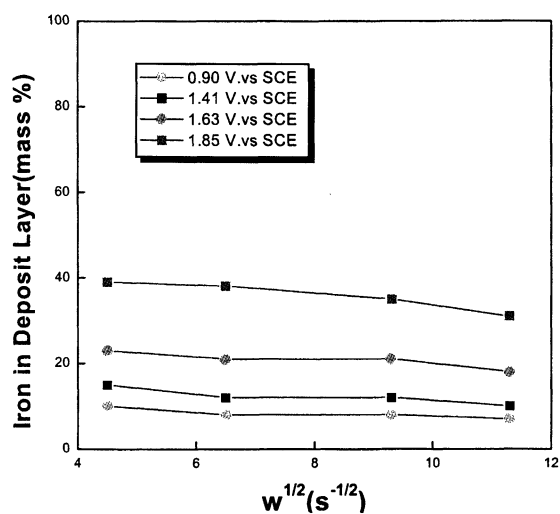

Fig. 9 The effect of voltage on the zinc content of electrodeposited Fe–Zn–P alloys.
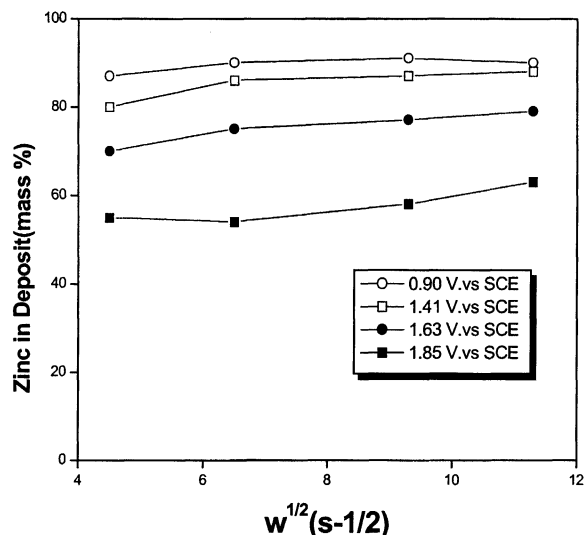

Fig. 7 The effect of rotating speed on the deposition rate constant of P at 313 K.

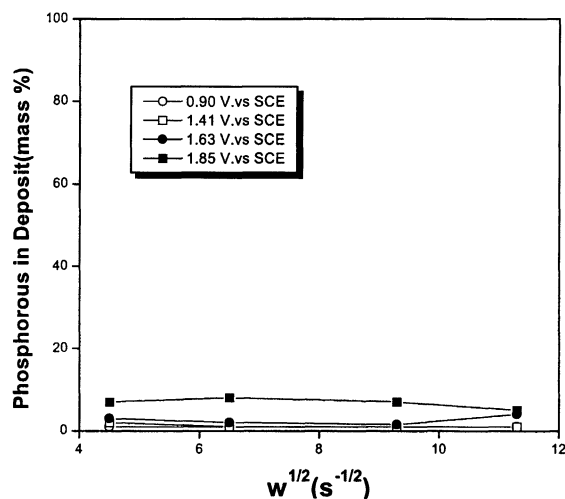Fig. 10 The effect of voltage on the phosphorus content of electrodeposited Fe–Zn–P alloys.

Fig. 8 The effect of voltage on the iron content of electrodeposited Fe–Zn–P alloys.
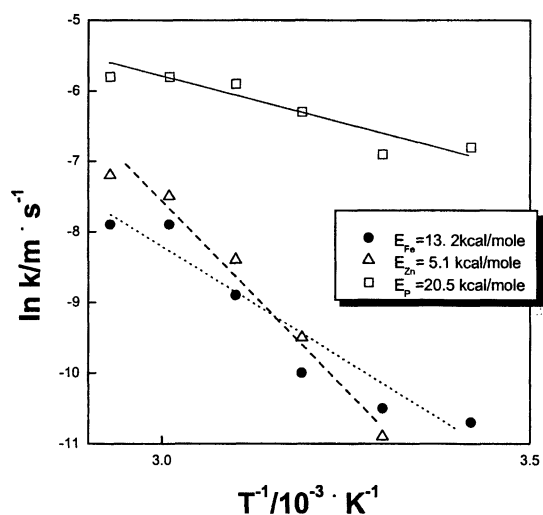

Fig. 11 Arrhenius plot for the electrodeposition of Fe–Zn–P coating at −1.41 V (vs. SCE), 400 min^{-1}.

5. Conclusion

(1)   Deposition rate of zinc and iron onto steel in Zn–Fe–P system was controlled by mass transfer and electrochemical reaction and those phosphorous were controlled by electrochemical reaction.

(2)   The zinc content in the Fe–Zn–P alloy increased but iron content decreased with stirring speed. The zinc content decreased but iron content increased with voltage. The phosphorus content is almost constant with respect to stirring speed in the lower voltage ranges and decreased slightly with stirring speed in the higher voltage ranges.

(3)   An anomalous codeposition was shown in the Fe–Zn–P ternary alloy system. To get Fe–Zn–P alloy coating in which the iron content was 15 to 20 mass%, the molar ratio of iron to zinc in the plating bath should be maintained at approximately 4.5.

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