The Process and Mechanism of Electrodepositing a Zn-Fe-SiO$_2$ Composite Coating

by Y. Zhang, Y. Fan,* X. Yang, Z. Chen & J. Zhang

Bright Zn-Fe-SiO$_2$ composite coatings have been produced by electrodeposition, and the influence of operating conditions on the coating composition and corrosion resistance have been studied. The results show that Zn-Fe-SiO$_2$ composite coatings are highly corrosion resistant without supplementary passivation (chromating). The corrosion resistance was about 1.5 to 4 times that of Zn-Fe coatings and about 3 to 20 times that of unalloyed zinc coatings. The corrosion resistance of Zn-Fe-SiO$_2$ coating was improved by increasing the SiO$_2$ content. The theory behind the SiO$_2$ co-deposition with the Zn-Fe alloy was studied, and a concept of a micro double layer is introduced. The mechanism of a cation-additive is analyzed, and a model describing the forces acting on SiO$_2$ particles near the cathode is also given. This theory is in accord with experimental results.

Electrodeposited composite coatings are of considerable importance in view of their unique mechanical and protective performance. They have been widely used in engineering applications.[1-6] There has been much research on zinc and zinc-based alloy coatings because they can be used as protective coatings on steel surfaces. However, most of these coatings are commonly passivated by a hexavalent chromate, which brings forth many problems related to waste disposal because of its high toxicity.[7-10] In the current work, a bright Zn-Fe-SiO$_2$ composite coating has been deposited, which is highly corrosion resistant without a passivation treatment.

Experimental procedure

The plating solution composition and operating conditions were as follows:

$FeSO_4 \cdot 7H_2O$,	120-200 g/L (16.0-26.7 oz/gal);
$ZnSO_4 \cdot 7H_2O$,	30-70 g/L (4.0-9.3 oz/gal);
$(NH_4)_2SO_4$,	80-120 g/L (10.7-16.0 oz/gal);
H_3BO_3,	30 g/L (4.0 oz/gal);
SiO_2,	20-60 g/L (2.7-8.0 oz/gal);
Citric acid,	30-50 g/L (4.0-6.7 oz/gal);
Cation-additive,	(proprietary);
pH,	2.0-4.0;
Current density,	4.0-8.0 A/dm^2 (37.2-74.3 A/ft^2);
Temperature,	15-25°C (59-77°F);
Agitation (rotation speed),	200 rpm.

In this work, 40 × 50 mm (~1.6 × 2.0 in.) low carbon steel was used as the cathode. Graphite, with like dimensions, was used as the anode. Ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and zinc sulfate ($ZnSO_4 \cdot 7H_2O$) were used as primary salts. Ammonium sulfate [$(NH_4)_2SO_4$] was used to enhance solution conductivity. Citric acid ($C_6H_8O_7 \cdot H_2O$) provides a ligand, while boric acid (H_3BO_3) acts as a buffer. Silica (SiO_2) particles are co-deposited with the zinc-iron alloy. The proprietary cation-additive promotes the co-deposition of the silica, while agitation keeps it suspended in solution.

In order to compare the corrosion resistance of the various coatings they were immersed in a 5% NaCl solution. The corrosion resistance was based on the time required to produce visible corrosion products.

Results & discussion

Influence of operating conditions on the composition of the coating

As shown in Fig.1, increasing the ferrous sulfate from 120 to 200 g/L (16.0 to 26.7 oz/gal), increased the iron content in the composite coating from 7.2% to 12.1%. When the ferrous sulfate was added, the ferrous ion concentration obviously increased, and the polarization for the deposition of iron decreased. Thus the iron content in the composite coating increased.

Figure 2 shows that the iron content in the composite coating decreased from 24% to 5.5% when the zinc sulfate

Nuts & Bolts: What This Paper Means to You

Plated zinc-iron alloy composites containing codeposited silica particles have been of interest as possible high-end cadmium substitutes, among other things. Here, their corrosion resistance, without supplemental chromating, is reported and compared with pure zinc and normal zinc-iron alloy coatings. Further, the authors propose a mechanism for how all of this works.

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* *Corresponding Author:*
Dr. Yunying Fan
Kunming University of Science and Technology
E-mail: yunyingfan7739@sina.com

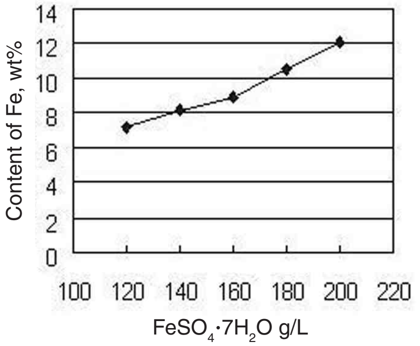

Figure 1—Influence of the concentration of $FeSO_4·7H_2O$ on the iron content in the coating.

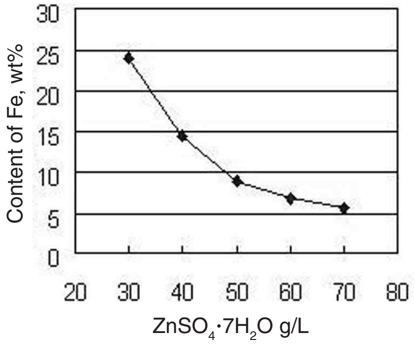

Figure 2—Influence of concentration of $ZnSO_4·7H_2O$ on the iron content in the coating.

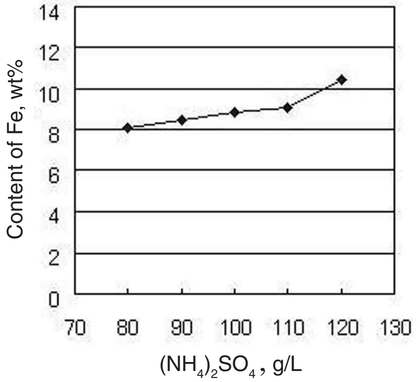

Figure 3—Influence of concentration of $(NH_4)_2SO_4$ on the iron content in the coating.

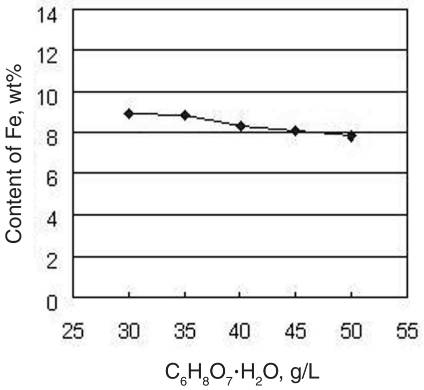

Figure 4—Influence of concentration of $C_6H_8O_7·H_2O$ on the iron content in the coating.

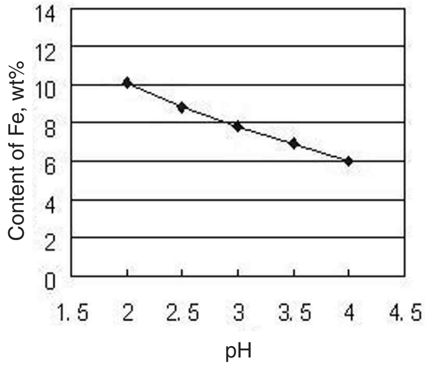

Figure 5—Influence of pH on the iron content in the coating.

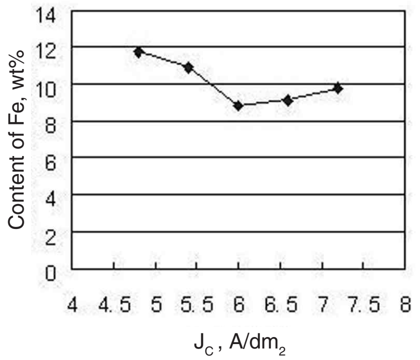

Figure 6—Influence of current density on the iron content in the coating.

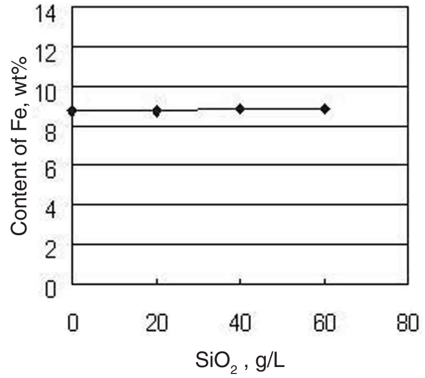

Figure 7—Influence of SiO_2 concentration on the iron content in the coating.

concentration was increased from 30 to 70 g/L (4.0 to 9.3 oz/gal). Similar to the effect with iron, increasing the zinc sulfate increased the zinc ion concentration in solution, and thus lowered the polarization for iron deposition. This favored zinc deposition, and the iron content of the composite coating decreased.

The influence of the ammonium sulfate concentration on the iron content is shown in Fig. 3. When the ammonium sulfate was increased from 80 to 120 g/L (10.7 to 16.0 oz/gal), the content of iron in the composite coating increased from 8.1% to 10.4%. The additional $(NH_4)_2SO_4$ increased the solution conductivity. The iron content increased because the ferrous sulfate concentration was greater than that of the zinc sulfate.

Figure 4 shows that the content of iron in the composite coating decreased from 9.0% to 7.9% when the citric acid concentration was increased from 30 to 50 g/L (4.0 to 6.7 oz/gal). Adding citric acid increased the cathodic polarization, favoring zinc deposition, and thus the iron content in the composite coating decreased.

As shown in Fig. 5, the content of iron decreased from 10.1% to 6.0% when the pH was increased from 2.0 to 4.0. Increasing the pH reduced the H^+ in solution, and citric acid provided more $C_6H_7O_7^-$, enhancing cathode polarization. In addition, when the pH was increased, Fe^{+2} was more readily oxidized to Fe^{+3}. For these two reasons, the iron content decreased with increasing pH.

The influence of current density on the iron content is shown in Fig. 6. As the current density was increased from 4.8 to 6.0 A/dm^2 (44.6 to 55.7 A/ft^2), the iron content decreased from 11.8% to 8.9%, and then increased to 9.7% with a further increase in current density to 7.2 A/dm^2 (66.9 A/ft^2). At the lower range of current density, the increase can reduce cathodic potential, favoring zinc deposition, and the iron content of iron decreased. At the higher range, however, above 6.0 A/dm^2 (55.7 A/ft^2), the iron content increased. Here, with the metal ions arriving at the cathode in large numbers, and with the concentration of ferrous sulfate greater than that of zinc sulfate, the content of iron increased.

Figure 7 shows the influence of silica content on the iron content in the coating. The iron content remained nearly stable, between 8.8 and 8.9%, with the addition of up to 60 g/L (8.0 oz/gal) of SiO_2. We surmise that the silica had no effect on the current distribution of zinc and iron at the cathode.

The influence of the concentration of SiO_2 in solution on the content of SiO_2 in the coating can be seen in Fig. 8. When the silica was increased from 20 to 60 g/L (2.7 to 8.0 oz/gal), the deposit content of SiO_2 increased from 0.40% to 0.51%, reaching a maximum. When the silica concentration increased, the amount of SiO_2 adsorbed at cathode increased, but it was physically limited, and thus the silica content reached the observed maximum.

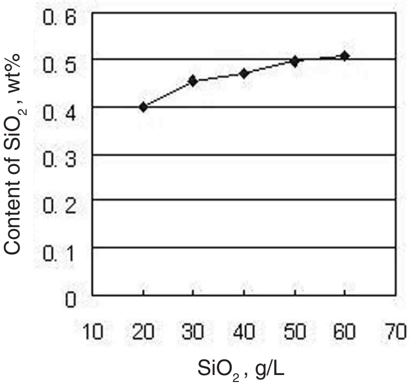

Figure 8—Influence of SiO_2 concentration on the SiO_2 content in the coating.

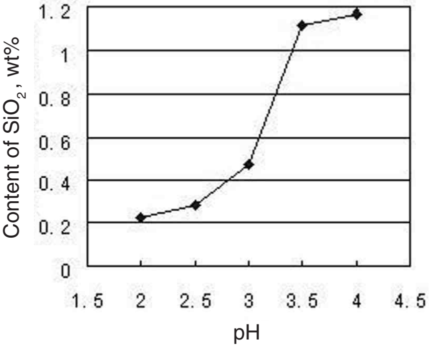

Figure 9—Influence of pH on the SiO_2 content in the coating.

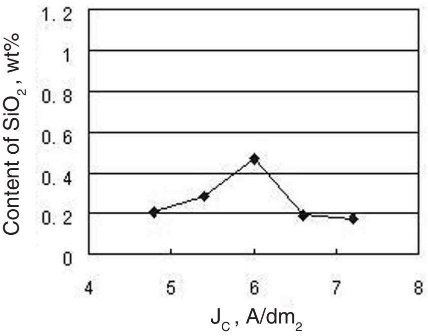

Figure 10—Influence of current density on the SiO_2 content in the coating.

Figure 9 shows the influence of pH on the SiO_2 content in the coating. When the pH increased from 2.0 to 4.0, the silica content increased from 0.22% to 1.17%, again reaching a maximum. When the pH increased, the amount of H_2 separated from the cathode decreased. At the same time, the metal hydroxides $Fe(OH)_2$ and $Zn(OH)_2$, which can absorb SiO_2 began to appear at the cathode. These two factors tended to increase the amount of SiO_2 adsorbed at the cathode. Again, it was limited, so the silica content increased to a maximum.

The influence of current density on the silica content in the coating is shown in Fig. 10. As the current density was increased from 4.8 to 6.0 A/dm^2 (44.6 to 55.7 A/ft^2), the silica content increased from 0.21% to 0.47%, and then decreased to 0.18% when the current density was further raised to 7.2 A/dm^2 (66.9 A/ft^2). At low current densities, the metal deposition velocity may have favored the co-deposition of silica. When the current density exceeded 6.0 A/dm^2 (55.7 A/ft^2), the extent that the current density promoted silica co-deposition may have reached its limit.

Corrosion resistance of the Zn-Fe-SiO_2 composite coating

In order to compare corrosion resistance of zinc, Zn-Fe alloy and Zn-Fe-SiO_2 composite coatings, specimens were immersed in 5% NaCl solution and the time required to form visible corrosion products was recorded. The results are shown in Table 1. It can be seen that the corrosion resistance of the Zn-Fe-SiO_2 composite was better than that of the Zn-Fe alloy coating, by a factor of 1.5 to 4. It was about 3 to 20 times better than the corrosion resistance of the pure zinc coating.

In 5% NaCl solution, the "rust" of the pure zinc coating was a white corrosion product, $Zn(OH)_2$ and its formation is described by the following reaction :

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2$$

The product of the Zn-Fe alloy coating is red, which may be either $Fe(OH)_2$ or $Fe(OH)_3$. This suggests that iron in coating may retard the formation of $Zn(OH)_2$. The formation of $Fe(OH)_2$ and $Fe(OH)_3$ was much slower than for $Zn(OH)_2$, and the corrosion resistance of the Zn-Fe coating was better than that of the zinc coating. As for the Zn-Fe-SiO_2 composite coating, the presence of silica reduced the portion of exposed interface between coating and the corroding medium, thus reducing the amount of oxygen penetrating into the coating.

In order to determine the influence of silica content on the coating corrosion resistance, five pieces of composite coated specimens containing different silica contents were immersed in 5% NaCl solution, and the results are shown in Table 2. It can be seen that the corrosion resistance of the Zn-Fe-SiO_2 composite coating improved with increasing silica content. The more SiO_2 in the coating, the less exposed interface between the coating and the corroding medium, and less oxygen penetrated the coating.

Table 1

Comparison of Corrosion Resistance Between the Zn, Zn-Fe and Zn-Fe-SiO_2 Coatings

Category	Time to appearance of first corrosion (hr)	Time to appearance of 50% corrosion (hr)	Time to appearance of 90% corrosion (hr)
Zn	13	166	326
Zn-Fe Fe = 8.86 wt%	66	426	579
Zn-Fe-SiO_2 Fe = 8.86 wt% SiO_2 = 0.47 wt%	256	579	1150

Mechanism of the cation-additive

Considerable research on how particles co-deposit with metals has been accomplished, but there are many factors which can affect composite electrodeposition. The systems studied encompass a wide variety of electrolytes and a wide variety of operating conditions, and thus there is no unified theory as to the composition and structure of composite coatings.[11,12] In spite of this situation, there is agreement that the process of composite electrodeposition is composed of three steps:

1. Particles are transported to the cathode. This step mainly depends on agitation, cathode shape and the forces between the particles and cathode.

2. Particles adhere to the cathode. This step is affected by factors that can influence the forces between the particles and cathode.

3. Particles are enclosed by the depositing matrix metal(s). This step is determined by how strongly the particles adhere to the cathode, how the flowing solution impacts the particles and how fast the matrix metal deposits at the cathode.

It can be seen from these three steps that the force between the particles and cathode plays a key role in composite electrodeposition, and studying this force is important.

According to reports, some abio- or inorganic ions, such as Tl^+, Cs^+ and NH_4^+, can be easily adsorbed by the particles, and thus such ions are called "cation-additives."[1,10,12] It is thought that cation-additives can enhance the static forces between the particles and the cathode, but there has been no in-depth research on cation-additives. In order to study the mechanism of composite electrodeposition more thoroughly, the mechanism behind the action of cation-additives during composite electrodeposition was studied. The concept of a "micro double layer" is brought forward for the first time. After analyzing the structure of the micro double layer near the surface of the silica particles and how the static potential is distributed in the layer, a model was developed which describes the forces acting on the SiO_2 particles near the cathode. This model can be used to explain the mechanism of cation-additives during composite electrodeposition.

The composition of composite coatings from electrolytes with and without a cation-additive was compared, and the results are shown in Table 3. It can be seen that silica will not be co-deposited unless there is some amount of cation-additive in solution. Thus, the presence of a cation-additive is indispensable to depositing Zn-Fe-SiO_2.

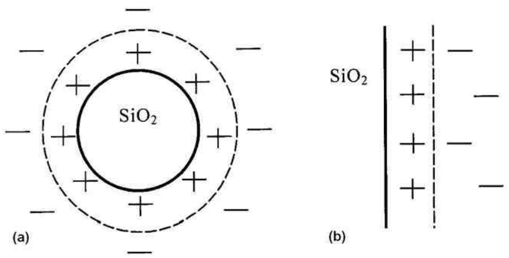

Figure 11—Double layer formation between the surface of the particle and the solution. (a) macro double layer; (b) micro double layer.

After an SiO_2 particle absorbs some abio-ions, a double layer will form between the surface of the particle and the solution. From a macro standpoint, the spherical double layer formed between the surface of the particle and the solution differs from a conventional double layer formed between the electrode and solution, as shown in Fig.11a. However, the diameter of the SiO_2 particles used in this research was 0.76 μm (~30 μ-in.), while the diameter of an abio-ion is about 0.03 to 0.17 $\times 10^{-3}$ nm (1.2 to 6.9 $\times$ 10^{-6} μ-in.),[13] so the surface of a silica particle can be seen to be a surface for a small group of abio-ions. Therefore, the double layer formed near the particle surface resembles a normal double layer from micro standpoint, as shown in Fig.11b. For the moment, let us define this as a micro double layer.

Because the quantity of ions absorbed on the particle surface varies, the structure and distribution of the static potential of the micro double layer also vary. According to electrochemical theory,[14] if the solution is watery, the diffusion layer will be thick, and the structure and distribution of the static potential of the micro double layer would be that shown in Fig. 12a. If the solution is denser, the diffusion layer will be thinner. The structure and distribution of the static potential of the micro double layer would be as

Table 2
Influence of the SiO_2 Content on the Corrosion Resistance of the Zn-Fe-SiO_2 Coating

Fe, wt%	SiO_2, wt%	Time to appearance of first corrosion (hr)	Time to appearance of 50% corrosion (hr)	Time to appearance of 90% corrosion (hr)
8.86	0.40	209	504	1119
8.86	0.45	226	529	1144
8.86	0.47	256	579	1150
8.86	0.49	362	725	1264
8.86	0.51	426	812	1332

Table 3
Influence of the Cation-additive on the SiO_2 Content in the Coating

Cation-additive in solution	Iron content in the coating (wt%)	Silica content in the coating (wt%)
None	7 - 12	0.0
Proprietary	7 - 12	0.2 - 1.2

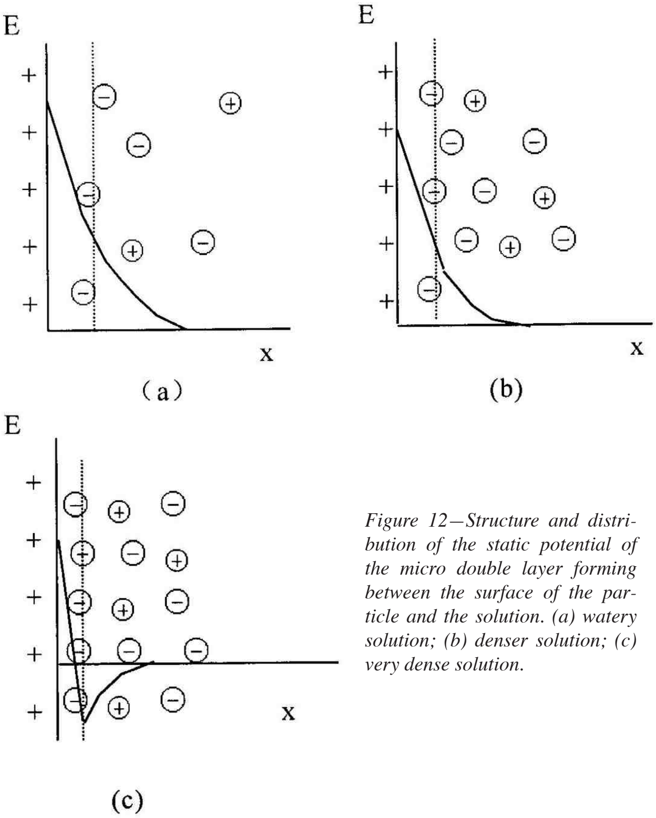

Figure 12—Structure and distribution of the static potential of the micro double layer forming between the surface of the particle and the solution. (a) watery solution; (b) denser solution; (c) very dense solution.

shown in Fig. 12b. If the solution is very dense and there is specific adsorption of anions, the diffusion layer will be very thin, and the structure and distribution would be as shown in Fig. 12c.

In this study, the anions present are primarily SO_4^{-2} and OH^-. For SO_4^{-2}, the specific adsorption is negligible.[14] The concentration of OH^- is very low, less than 1×10^{-10} mol/L, so it is impossible that the structure and the distribution of the static potential of the micro double layer will be like that in Fig. 12c. In the case of Fig. 12a or b, the potential gradient of the micro double layer is weak, so this layer can be destroyed by the presence of other ionic species.

When other ions are inserted into the micro double layer, the SiO_2 particle will co-deposit with the matrix metal like a cation. There are four forces to which the SiO_2 particle will be subject, as shown in Fig. 13a. F denotes the force arising from solution flow, f denotes the force arising from the depositing matrix metal, Q denotes the repulsive force caused by other cations in solution and N denotes the attractive force caused by the cathode. The first two forces (F and f) will repel the SiO_2 particle away from cathode, but the latter two forces (Q and N) will attract it, so the SiO_2 particle can adhere to the cathode and be surrounded by depositing metal. If there is no cation-additive in solution, the silica particle will absorb no cations. It will be only subject to the F- and f-forces, as shown in Fig. 13b, and it will barely be co-deposited into the coating.

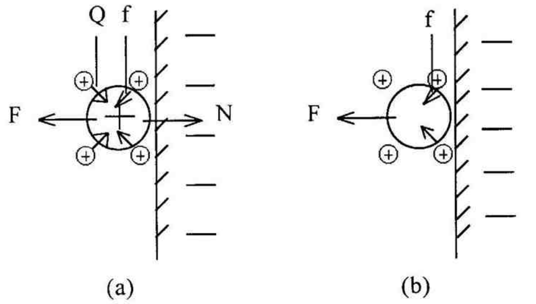

Figure 13—Model of the forces acting on an SiO_2 particle near the cathode. (a) SiO_2 absorbing cations; (b) SiO_2 absorbing no cations.

Conclusions

The concentration of primary salt, pH and current density are the primary factors influencing the iron content in electrodeposited Zn-Fe-SiO_2 composite coatings, and the pH primarily affects the silica content.

The Zn-Fe-SiO_2 composite coating is highly corrosion resistant and requires no post-passivation. Its corrosion resistance is about 1.5 to 4 times that of a Zn-Fe alloy coating and about 3 to 20 times of that of a pure zinc coating. The corrosion resistance of the composite coating can be improved by increasing the SiO_2 content.

A cation-additive is essential to the co-deposition of SiO_2 particles in the Zn-Fe alloy. A model of the forces acting on the silica particles near the cathode can explain the mechanism involving the action of the cation-additive during composite electrodeposition.

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Zhang


Fan


Yang


Chen

About the Authors

Dr. Yingjie Zhang is a Professor at Kunming University of Science and Technology. She has worked in electrochemistry and the metal finishing industry for about 20 years and has published one monograph and more than 30 papers.

Dr. Yunying Fan is studying at Kunming University of Science and Technology. His areas of research include zinc alloy and composite plating. He has worked in metal finishing for four years and has published ten papers.

Dr. Xianwan Yang is a Professor at Kunming University of Science and Technology. He has worked in the area non-ferrous metallurgy for more than 40 years and has published eight monographs and more than 140 papers. He is a well-known expert on hydrometallurgy in China.

Zhen Chen is a lecturer at Kunming University of Science and Technology. His major areas of research and teaching are in electrochemistry and inorganic chemistry. He has worked in metal finishing for three years and has published three papers.