Effect of SiO_2 Colloid on the Electrodeposition of Zinc-Iron Group Metal Alloy Composites

A. Takahashi,* Y. Miyoshi, and T. Hada

Nippon Steel Corporation, Steel Research Laboratories, 20-1 Shintomi, Futtsu, Chiba 299-12, Japan

ABSTRACT

The mechanism of codeposition in Zn-based composite platings has yet to be clarified in detail. In this study, electrodeposition of Zn-Fe group metal-SiO_2 composite was performed from the electrolytes containing Zn, Fe group metal cations, and SiO_2 colloid. An induced codeposition was found between Fe group metal and SiO_2 colloid. This result is explained from the adsorption of Fe group metal ions on SiO_2 colloid and the agglomeration of SiO_2 colloid on the cathode. Extending this knowledge to the Zn-Cr-SiO_2 system composites contain Cr and SiO_2 contents of up to 18 and 10 weight percent, respectively, have been obtained for the first time. In this system, SiO_2 catalyzed the Cr codeposition. These composites showed excellent corrosion resistance.

Zinc-based composite plating has been investigated as a means of making sheet steel corrosion resistant. Zn-Ni-SiO_2 [1] and Zn-SiO_2 [2] systems have been introduced. These were electrodeposited from electrolytes containing metal cations and SiO_2 colloid of 20 nm average diameter. Clarifying the codeposition mechanism is very important, because it can help to control the plating structure, and hence the plating properties. The codeposition mechanism of particles of metal-oxide or carbide of 1 to 3 μm diam range, has been previously studied. Guglielmi proposed a mechanism[3] which explained the codeposition behavior of Ni-SiC or Ni-TiO_2 systems. The códeposition process at the cathode/electrode interface is described mathematically, based on two successive adsorption steps, the weak and the strong adsorption steps, which are similar to the physical and chemical adsorption of gas at a solid surface. However, the codeposition behavior of the Zn-SiO_2 colloid systems is different from that found by Guglielmi probably because the SiO_2 colloid has a smaller size and peculiar chemical properties compared with the oxide or carbide powders studied in his system. The mechanism of SiO_2 colloid codeposition has yet to be clarified in detail.

A variety of electrodeposited zinc-based alloys have been introduced.[4] Although Zn-Cr alloy cannot be easily obtained by aqueous electrodeposition, it is expected to exhibit excellent corrosion resistance due to Cr. Recently, one of our research groups demonstrated electrodeposition of Zn-Cr alloy from electrolyte containing special additives.[5]

In the present study, the codeposition mechanism of Zn-Fe group metals-SiO_2 systems was investigated. Then it was applied to the Zn-Cr-SiO_2 system for studying the possibility of its electrodeposition.

Experimental

Electrodepositions were carried out onto cold-rolled steel sheets of 100 × 200 mm cross section and 0.8 mm in thickness, using a circulation cell. Electrolytes were acidic sulfate baths containing SiO_2 colloid and cations of Zn, Fe, Ni, Co, and Cr. SiO_2 colloid is Cataloid-SN (Shokubai-Kasei), containing 20 weight percent (w/o) of SiO_2 and less than 0.05 w/o of Na_2O. The colloid size is 10 to 20 nm. Other reagents such as zinc sulfate heptahydrate are G. R. grade. The bath temperature is 323 K with a pH of 2.0. Table I shows the bath compositions. The concentrations of Fe-, Ni-, Co-, Cr cations, and SiO_2 colloid were varied in a wide range.

A current density of 100 A/dm^2 was employed, and the other electrodeposition conditions are listed in Table II.

Deposits obtained were studied with the following methods. Chemical compositions were determined by wet chemical analysis. Depth profiles were analyzed by glow discharge spectrometry (GDS). Cross-sectional microstructure was studied by transmission electron microscopy (TEM) equipped with an ultrathin window-energy dispersive spectrometry (UTW-EDS). The thin sectional specimens for TEM observations were prepared by the ultramicrotomy.[6] The chemical state of the Zn-Cr alloy was studied by x-ray photoelectron spectroscopy (XPS), and the crystal structures were analyzed by x-ray diffraction (XRD).

The zeta potential of SiO_2 colloid at various pH levels was measured by Pen-Kem, Incorporated, Lazer Zee Meter Model 501. Colloid concentration was 10 g/liter and pH was adjusted by the addition of H_2SO_4 and NaOH.

The corrosion resistance was evaluated in a cyclic corrosion test (CCT). The CCT conditions are shown in Table III.

Bare sheets of 70 × 150 mm in size served as specimens. After 14 cycles in the CCT, the corrosion products and the remaining deposits were removed by pickling, and the weight loss of the steel stubstrate was measured.

Results and Discussion

Codeposition behavior of Zn-Fe group metal-SiO_2 systems.—Figure 1 shows the relationship between the SiO_2 colloid concentration in the bath and the plating composition of the Zn-Fe, Zn-Ni, and Zn-Co systems. Composite platings would be obtained from the electrolytes containing SiO_2 colloid. The SiO_2 contents in the deposits increased with an increase in its concentration in the bath. Although the concentration of metal cations was kept constant, Fe group metal contents in the deposits significantly increased with an increase in the SiO_2 colloid concentration. For example, in the Zn-Fe systems, the Fe content increased from 10 w/o using the SiO_2 colloid-free bath to 22 w/o using the 60 g/liter bath. This indicates that SiO_2 colloid accelerates the electrodeposition of Fe group metals. The effect of Fe group metal cation concentration in the bath on the SiO_2 codeposition was also studied. According to Fig. 2, SiO_2 codeposits only slightly from the pure zinc sulfate bath, and the addition of Fe group metal ions in the zinc bath increases the codeposition rate rapidly. This means that Fe

Table I. Bath compositions.

$ZnSO_4 \cdot 7H_2O$	1 mol/liter
$FeSO_4 \cdot 7H_2O$	0-0.7 mol /liter
$CoSO_4 \cdot 7H_2O$	0-0.7 mol /liter
$NiSO_4 \cdot 6H_2O$	0-0.7 mol /liter
$Cr_2(SO_4)_3 \cdot nH_2O$	0-0.9 mol /liter
SiO_2 colloid (Cataloid-SN)	0-300 g/liter
pH	2.0
Temperature	323 K

Table II. Electrodeposition conditions.

Current density	100 A/dm^2
Flow rate (circulation cell)	100 m/min
Anode (100 × 200 mm)	Pt plated Ti sheet
Cathode (100 × 200 mm)	Steel
Coating weight	20 g/m^2

* Electrochemical Society Active Member.

Table III. CCT condition.

→SST (308 K, 5% NaCl) ↓	6 h
Dry (343 K, RH 60%) ↓	4 h
Humidify (322 K, RH 95%) ↓	4 h
└Freeze (253 K)	4 h

SST: salt spray test.

group metal cations accelerate the codeposition of SiO_2. Fe group metal cations and SiO_2 colloid must be increased codeposition. In other words, these systems show the induced codeposition. For a further understanding of this phenomena, the structure of Zn-22 w/o Fe-7 w/o SiO_2 composite coating was analyzed. This composite was selected for the analysis because it shows the strongest induced codeposition behavior. Figure 3 gives the TEM bright field image and UTW-EDS of the crosssection. The plating layer exhibits a laminar structure consisting of bright layers and dark layers with a thickness of a few hundred nanometers. The white particles in the bright layers have the same size as SiO_2 colloid added in the bath, and UTW-EDS measurements revealed the presence of Zn, Fe, Si, and O in them. In the dark layers, the white particle is not found and UTW-EDS showed only Zn and Fe peaks. From these observations it can be estimated that the bright one is a mixture of Zn-Fe alloy and aggregated SiO_2. On the other hand, the dark one consists only of Zn-Fe alloy. The Fe peak intensity from the SiO_2 aggregated layer is four times higher than the Zn-Fe alloy layer. This means that SiO_2 and Fe deposited at the same time and at the same place. This is a kind of induced codeposition. In an anomalous codeposition,[7] in which the electrochemically less noble Zn deposits preferentially than the more noble Fe, SiO_2 colloid acts to shift the anomalous codeposition to the normal deposition.

These results can be explained by the adsorption of Fe group metal ions on the SiO_2 and the agglomeration of SiO_2 colloid on the cathode.[1] Based on this theory, the codeposition mechanism of Zn-Fe group metals-SiO_2 systems can be drawn schematically as shown in Fig. 4. There are two kinds of pathways. The upper one in Fig. 4 is a typical alloying pathway. On the cathode, $Zn(OH)_2$ is formed due to the pH increase, which leads to anomalous codeposition. The lower one is an aggregating pathway. As the SiO_2 colloid has a negative zeta potential as shown in Fig. 5, its electrophoresis to the cathode cannot be expected. However, the preferential adsorption of Fe group metal cations on the colloid surface[1] brings about the electrophoresis. On the cathode, SiO_2 colloid easily agglomerates due to the pH increase, because this colloid is agglomerated at a neutral pH.[1] The agglomerated colloid may suppress the formation of $Zn(OH)_2$ probably by blocking the Zn ion diffusion to the cathode and realizing the normal codeposition. The preferential adsorption and the colloid agglomeration cause the induced codeposition.

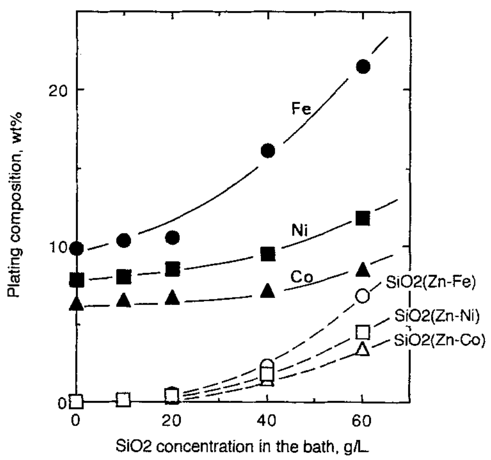

Fig. 1. Relationship between SiO_2 colloid concentration in the bath and plating compositions. $ZnSO_4 \cdot 7H_2O$ = 1.0 mol/liter, $FeSO_4 \cdot 7H_2O$ = 0.7 mol/liter, $CoSO_4 \cdot 7H_2O$ = 0.7 mol/liter, $NiSO_4 \cdot 6H_2O$ = 0.8 mol/liter. pH 2.0, Temp = 323 K, *Dk* = 100 A/dm^2, coating weight = 20 g/m^2.

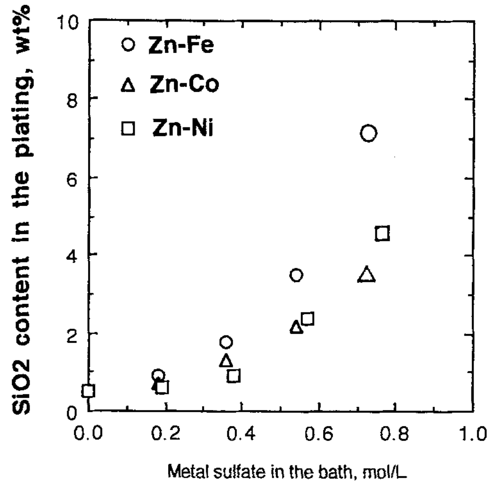

Fig. 2. Relationship between Fe group metal sulfate concentration in the bath and SiO_2 contents in platings. $ZnSO_4 \cdot 7H_2O$ = 1.0 mol/liter, SiO_2 = 60 g/liter. pH 2.0, Temp = 323 K, *Dk* = 100 A/dm^2, coating weight = 20 g/m^2.

Codeposition behavior of Zn-Cr-SiO_2 systems.—Considering the analogy between Fe and Cr, electrodeposition of Zn-Cr-SiO_2 composite plating was studied. Figure 6 shows the relationship between the SiO_2 colloid concentration in the Zn-Cr baths and the composition. The metal cation concentration in the bath was fixed. Both SiO_2 and Cr contents in the deposits increased with the increase in the SiO_2 colloid concentration. A small amount of Cr deposited from the SiO_2-free bath. The highest contents of Cr and SiO_2 were 18 and 10 w/o, respectively. These results indicate that the mechanism demonstrated in Fig. 4 can be applied to the electrodeposition of Zn-Cr-SiO_2 composite platings. The SiO_2 colloid functioned as a necessary additive required for the Cr codeposition.

Structure of Zn-13%Cr-8%SiO_2 composite.—Figure 7 shows the GDS depth profile of the composite. Zn, Cr, and SiO_2(Si) are distributed uniformly. XPS depth profiles of Zn and Cr are shown in Fig. 8. The chemical state of Zn after argon sputtering for more than 20 min is metallic and that of Cr is a mixture of metallic and a small amount of oxide. The electrolytic reduction of Cr^{3+} at the cathode was incomplete and some amount of oxide was included. Figure 9 gives the XRD spectrum from the surface of the composite. One sharp and intensive peak and two broad peaks were obtained. The d-value of the sharp peak is 2.100 which is very close to the 2.091 Å of Zn-eta(101). The shift of the d-value from 2.091 to 2.100 Å can be explained by the solid solution of Cr in the Zn-eta phase. The two broad peaks could not be indexed by the ASTM cards, which did not cover the Zn-Cr alloy system. These broad peaks could be estimated as resulting from the diffraction as nonequilibrium and/or nonregular structure of Zn-Cr alloy. Figure 10 shows a TEM bright field image of a cross section of Zn-13%Cr-8%SiO_2 plated steel sheet. The white particles of SiO_2 are seen to be almost uniformly distributed in the plating. A laminar structure similar to that of Zn-Fe-SiO_2 in Fig. 3 was scarcely observed.

Results of GDS, XPS, XRD, and TEM indicate that the composite has a structure summarized as follows: (*i*) consists of Zn-eta phase, Zn-Cr alloy, Cr oxide, and SiO_2; (*ii*) the Zn-eta phase may contain a small amount of Cr; (*iii*) the Zn-Cr alloy might have a nonequilibrium and/or nonregular structure.

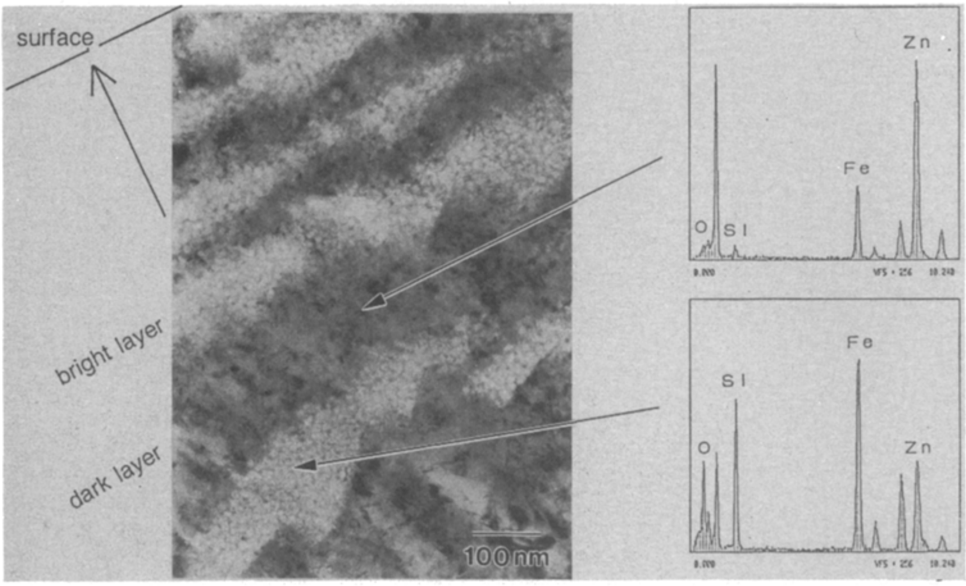

Fig. 3. Cross-sectional TEM-bright field image and UTW-EDS of Zn-22 w/o Fe-7 w/o SiO_2 composite plating.

Corrosion resistance of the composites.—Figure 11 shows the corrosion resistance of the Zn, Zn-Fe, Zn-Fe-SiO_2, and Zn-Cr-SiO_2 coated steel sheets without painting. In comparison with Zn-15Fe alloy coated steel sheet, Zn-22 w/o Fe-7 w/o SiO_2 showed a slightly better corrosion resistance. Zn-13 w/o Cr-8 w/o SiO_2 showed an excellent behavior. From these results, it can be concluded that SiO_2 has only a small effect on the corrosion resistance and the

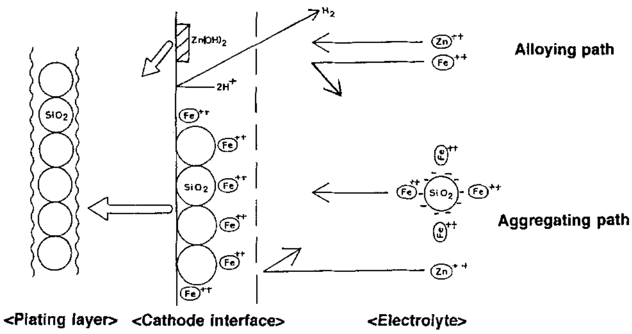

Fig. 4. Schematic diagram of the codeposition mechanism of Zn-Fe group metals-SiO_2 systems.

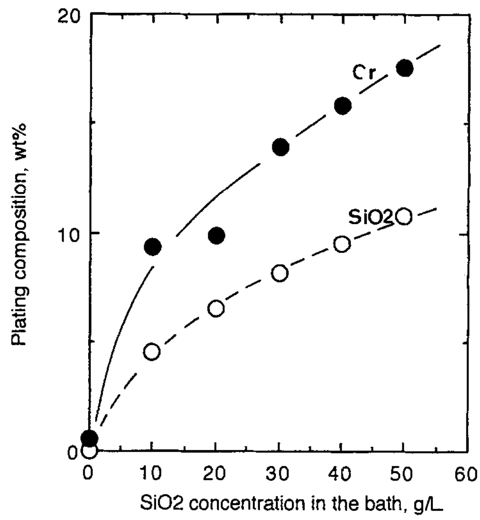

Fig. 6. Relationship between SiO_2 colloid concentration in the bath and plating compositions. $ZnSO_4 \cdot 7H_2O$ = 1.0 mol/liter, $Cr_2(SO_4)_3 \cdot nH_2O$ = 0.9 mol/liter. pH 1.5, Temp = 323 K, *Dk* = 150 A/dm², coating weight = 20 g/m².

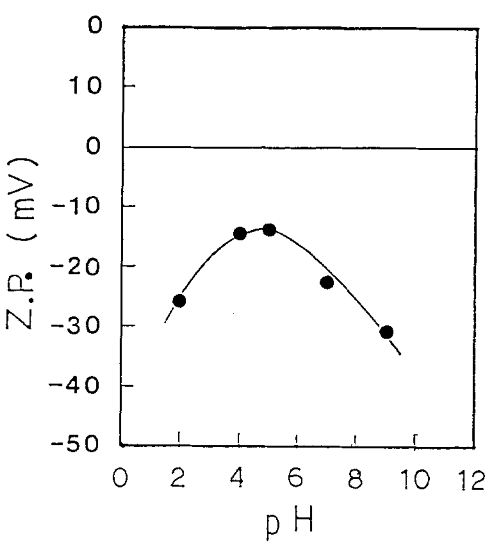

Fig. 5. Zeta potential of SiO_2 colloid in water.

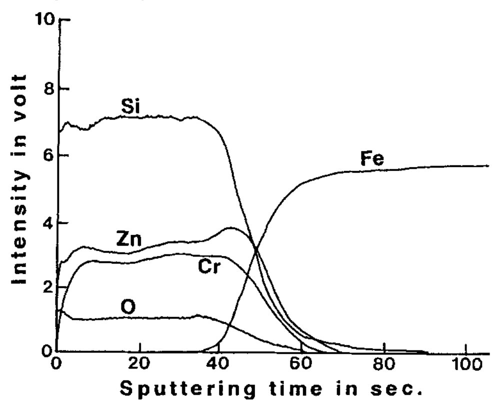

Fig. 7. GDS depth profile of Zn-13 w/o Cr-8 w/o SiO_2 composite plating.

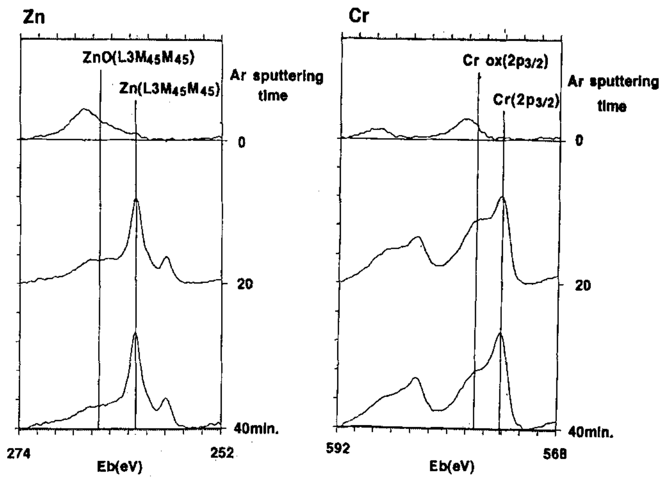

Fig. 8. XPS depth profiles of Zn-13 w/o Cr-8 w/o SiO_2 composite plating.

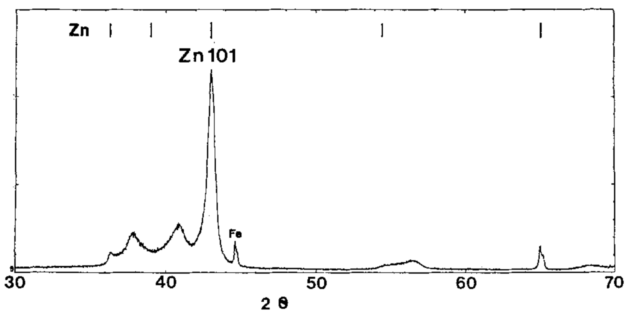

Fig. 9. XRD spectrum obtained from Zn-13 w/o Cr-8 w/o SiO_2 composite plating.

effect of Cr is remarkably large. In the Zn-based alloy-SiO_2 systems, SiO_2 plays an important role in promoting the codeposition of Cr rather than in the improvement of the corrosion resistance.

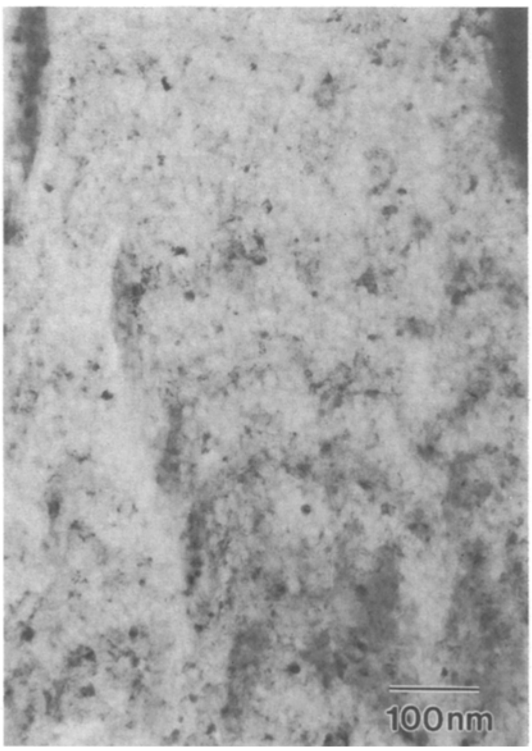

Fig. 10. Cross-sectional TEM-bright field image of Zn-13 w/o Cr-8 w/o SiO_2 composite plating.

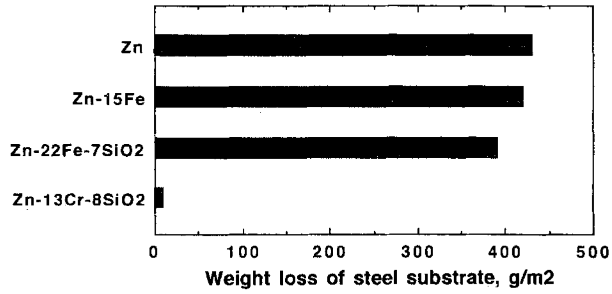

Fig. 11. Weight loss of steel substrate after CCT XIV cycles. Bare sheets coating weight is 20 g/m^2.

Conclusions

Zn-Fe group metals-SiO_2 composite platings were electrodeposited from the acidic sulfate baths containing metal ions and SiO_2 colloid of 20 nm in average diameter. Deposits obtained were studied with wet chemical analysis, GDS, TEM, XPS, and XRD. Codeposition behavior of the Zn-Fe group metals-SiO_2 colloid composites are summarized as follows:

1. An induced codeposition was found between Fe group metal ions and SiO_2 colloid.
2. The cross section of the Zn-22 w/o Fe-7 w/o SiO_2 composite plating had a laminar structure consisting of bright layers and dark layers with a thickness of a few hundred nanometers. The bright one is a mixture of Zn-Fe alloy and aggregated SiO_2, while the dark one consists only of Zn-Fe alloy.
3. The Fe peak intensity of UTW-EDS from the SiO_2 aggregated layer is four times higher than the Zn-Fe alloy layer.
4. The codeposition behavior was explained from the adsorption of Fe group metal ions on SiO_2 colloid and agglomeration of SiO_2 colloid on the cathode.

Considering the analogy between Fe and Cr, electrodeposition of Zn-Cr-SiO_2 composite platings was studied. Codeposition behavior and structure of composite platings are summarized as follows:

1. Composite platings with Cr and SiO_2 contents of up to 18 and 10 w/o, respectively, were obtained.
2. SiO_2 colloid proved to be necessary in order to obtain Zn-Cr alloy electrodeposition.
3. Zn-13%Cr-8%SiO_2 composite plating consisted of Zn-eta phase, Zn-Cr alloy, Cr oxide, and SiO_2. The Zn-eta phase may contain a small amount of Cr. Zn-Cr alloy might have a nonequilibrium and/or nonregular structure.

Corrosion resistance of the composite was studied.

1. The Zn-Fe-SiO_2 composite showed a slightly better corrosion resistance than the Zn-Fe alloy.
2. The Zn-Cr-SiO_2 composite showed excellent corrosion resistance. The SiO_2 had only a small effect on the corrosion resistance, and the effect of Cr was remarkably large.

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