Electrodeposition of Gradient Zinc Alloys

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An electrodeposition study of gradient zinc alloys onto steel has been carried out using a rotating disc electrode. The effects of rotation speed and potential on the composition of the alloy coatings were studied. The corrosion resistance and adhesion of the gradient zinc alloy coatings were compared with those of conventional duplex coatings. The zinc content of zinc-nickel (Zn-Ni) and zinc-iron (Zn-Fe) deposits increased with increasing rotation speed and applied voltage. Increasing the rotation speed increased the zinc content in zinc-nickel-phosphorus (Zn-Ni-P) deposits, and both nickel and phosphorus declined. The zinc-iron-phosphorus (Zn-Fe-P) system behaved differently in that the zinc content increased with increasing applied voltage. The corrosion resistance and deposit adhesion for all four gradient zinc alloys were superior to those of conventional duplex zinc alloys.

Zinc-based alloy coatings have been widely used to provide better corrosion protection than that provided by pure-zinc electrogalvanized deposits. Zinc-nickel (Zn-Ni) and zinc-iron (Zn-Fe) alloy electrodeposits have recently been commercialized and deposits comprised of two layers, with high and low zinc contents, have also been found to provide improved weldability and paintability.[1] Duplex Zn-Fe coatings, consisting of an underlayer containing 10 to 20% Fe and a top layer of 80 to 90% Fe, have been developed. The corrosion resistance of the duplex deposits has been reported to be excellent.[2,3]

The sudden change in composition at the interface between the two alloy deposits, however, has the potential for weak adhesion. A gradient alloy deposit may provide a solution to this problem. Little information is available on such alloys, whose composition changes continuously through the layer. In this paper, rotating disc studies were used in order to determine the electrochemical reaction mechanism and how it is affected by solution agitation, voltage and current density. In this work, we found that the metal content of the alloy was changed by rotation speed and voltage. With those results, we were able to produce gradient alloy deposits by continuously varying the rotation speed and applied voltage.

Experimental Procedure

Plating experiments were carried out in batches in a 1-L glass vessel, using a 3.0-cm diameter steel disc mounted on a Teflon holder. The setup is shown schematically in Fig. 1. The rotation speed of the disc was varied from 200 to 1200 RPM with an electrode rotator. A worm-gear apparatus achieved the continuous change in rotation speed. A power supply, a potentiostat and a function generator controlled the voltage. A standard saturated calomel electrode (SCE), equipped with a Luggin capillary probe, was positioned close to the rotating disc. A pure platinum anode was positioned 3.0 cm below the rotating disc in the plating solution.

The plating bath compositions used are shown in the table. A 500-mL plating solution was prepared with deionized water, and the solution temperature was controlled within 0.2°C using a constant temperature bath.

The deposit compositions were determined with an electron probe microanalyzer (EPMA), and the microstructure and surface morphology were determined by scanning electron microscopy (SEM). Results of adhesion and ductility tests were compared with those for conventional duplex alloys.

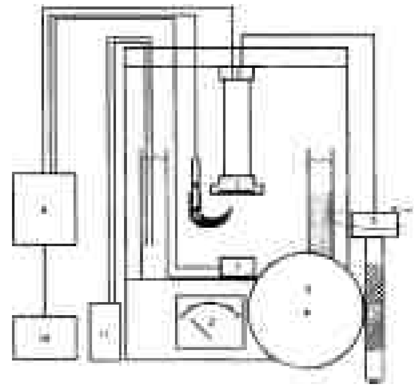

Fig. 1—Experimental apparatus for electrodepositing gradient zinc alloys

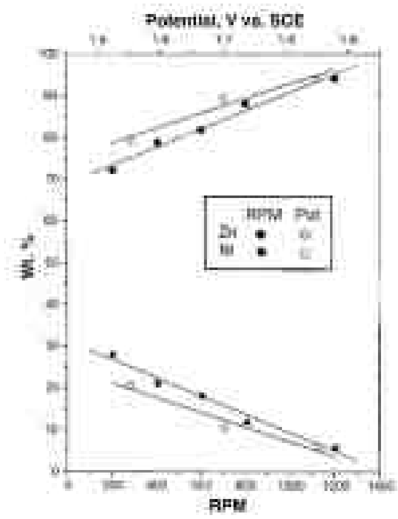

Fig. 2—Effect of rotation speed and potential on Zn and Ni composition in Zn-Ni coatings.

Results & Discussion

Gradient Zn-Ni & Zn-Fe Alloy Deposits

The effects of rotation speed and applied potential on the metal composition in Zn-Ni alloy deposits are shown in Fig. 2. Increasing the rotation speed and applied voltage increased the zinc content in the Zn-Ni system. This result arises from the fact that the zinc deposition is under mass transfer control. Increasing the rotation speed replenishes the cathode diffusion layer with zinc ions, and so the zinc content is increased. We also observed, however, that the rate of nickel deposition was much lower than zinc (anomalous codeposition) and was little affected by rotation speed, even at higher voltages.[4] From these results, it was possible to produce gradient Zn-Ni alloy deposits by continuously changing the rotation speed and bath voltage, as shown in Fig. 3. The EPMA photomicrographs show that the zinc content was gradually increased with a corresponding decline in nickel content as the rotation speed went from 200 to 1200 RPM. Similar results were obtained at a constant 400 RPM and an increase in applied voltage from 2.29 to 2.90 V (vs. SCE).

A similar phenomenon was observed in the Zn-Fe system. The zinc content increased with rotation speed, while the balance of iron decreased, as in Fig. 4. The corresponding

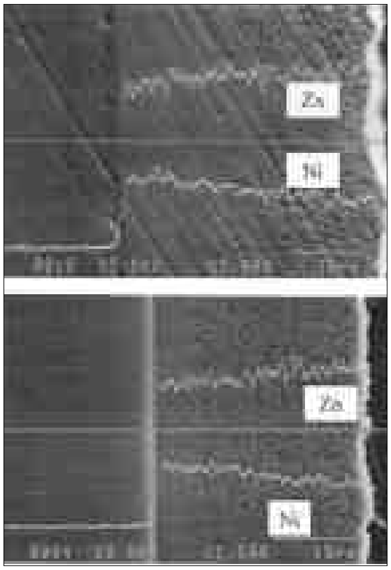

Fig. 3—Qualitative analysis of the plated Zn-Ni alloys by EPMA with (top) changing rotation speed from 200 to 1200 RPM at 2.51 V (vs. SCE) and 30ºC and (bottom) changing cathode potential from 2.29 to 2.90 V (vs. SCE) at 400 RPM and 30ºC.

Standard Compositions of Plating Baths

Zn-Ni		Zn-Fe		Zn-Ni-P		Zn-Fe-P	
$ZnCl_2$	40 g/L	$ZnCl_2$	140 g/L	$NiCl_2$	232 g/L	$ZnCl_2$	27 g/L
$NiSO_4$	90 g/L	$FeCl_2$	40 g/L	$ZnCl_2$	12.3 g/L	$FeCl_2$	179 g/L
$NiCl_2$	10 g/L	KCl	120 g/L	NaH_2PO_2	21.4 g/L	KCl	100 g/L
H_3BO_3	20 g/L	USS – P	3 mL/L	NH_4Cl	20 g/L	NH_4Cl	20 g/L
Sodium gluconate	60 g/L	Citric acid	2 g/L	Sodium citrate	29.4 g/L	NaH_2PO_2	22 g/L
						Sodium citrate	29 g/L

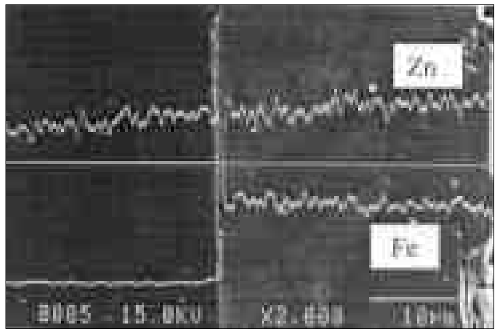

Fig. 5—Qualitative analysis of the plated Zn-Fe alloys by EPMA with changing rotation speed from 200 to 1200 RPM at 1.62 V (vs. SCE) and 60ºC.

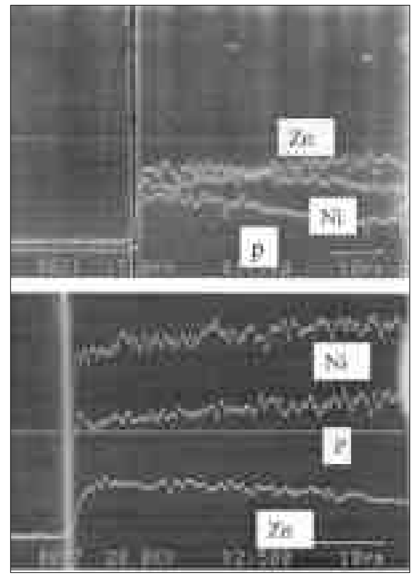

Fig. 7—Qualitative analysis of the plated Zn-Ni-P alloys by EPMA with (top) changing rotation speed from 200 to 1200 RPM at 1.62 V (vs. SCE) and 45ºC and (bottom) changing cathode potential from 1.06 to 1.95 V (vs. SCE) at 400 RPM and 45ºC.

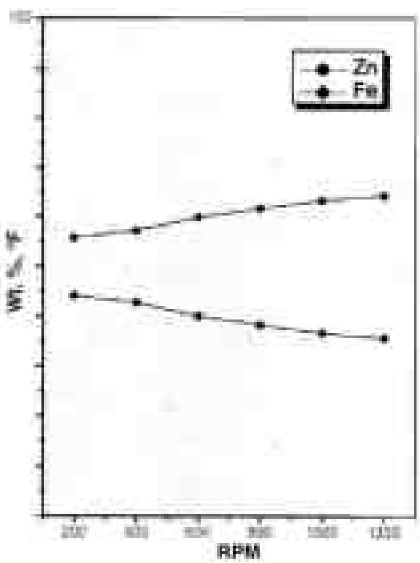

Fig. 4—Effect of rotation speed on the Zn and Fe composition in Zn-Fe coatings.

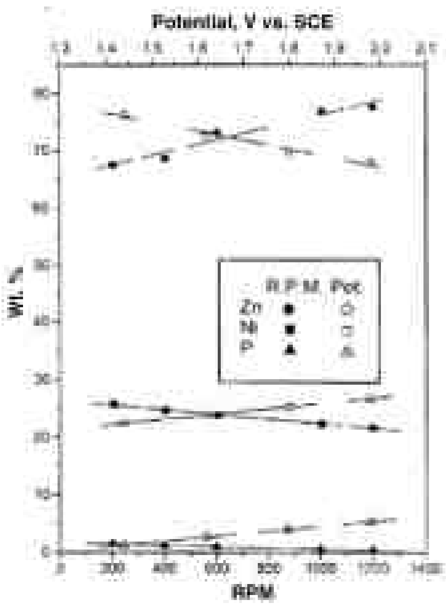

Fig. 6—Effect of rotation speed and potential on Zn, Ni and P composition in Zn-Ni-P coatings.

photomicrograph of Fig. 5 shows a gradual increase in zinc content and a decrease in iron. Again the rotation speed was continuously increased from 200 to 1200 RPM.

Gradient Zn-Ni-P & Zn-Fe-P Alloy Deposits

As was the case with the binary Zn-Ni and Zn-Fe systems, raising the rotation speed increased the zinc content in the ternary Zn-Ni-P system, but decreased both the nickel and phosphorus content, as seen in Fig. 6. The mechanism noted with the binary alloys also applies here, since the rate of zinc deposition for the Zn-Ni-P system is also observed to be under mass transfer control.[5] However, raising the applied voltage decreased the zinc content, but increased the nickel and phosphorus (Fig. 6). The similar trend for both the phosphorus and nickel can be attributed to an induced codeposition mechanism. The EPMA photomicrographs of the gradient Zn-Ni-P deposits are shown in Fig. 7. In the top figure, the zinc content gradually increased with rotation speed, but the nickel and phosphorus fell as one moved from the steel substrate to the deposit surface. The reverse effect was noted with increasing bath potential, noted in the bottom photomicrograph of Fig. 7.

The EPMA photomicrograph of a Zn-Fe-P alloy in Fig. 8 shows that the zinc content decreased, but the iron and phosphorus decreased outward from the substrate interface by raising the applied potential from 0.90 to 1.85 V.

X-ray Analysis of Zn-Ni Alloys

As shown in Fig. 9, the γ phase was observed at lower rotation speeds, in the range of 200 to 400 RPM. The η phase, containing a higher zinc content, appeared at higher rotation speeds, in the range of 800 to 1200 RPM.

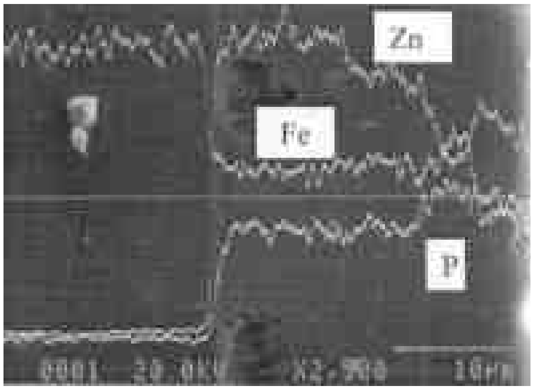

Fig. 8—Qualitative analysis of the plated Zn-Fe-P alloys by EPMA with (top) changing cathode potential from 0.90 to 1.85 V (vs. SCE) at 400 RPM and 40ºC.

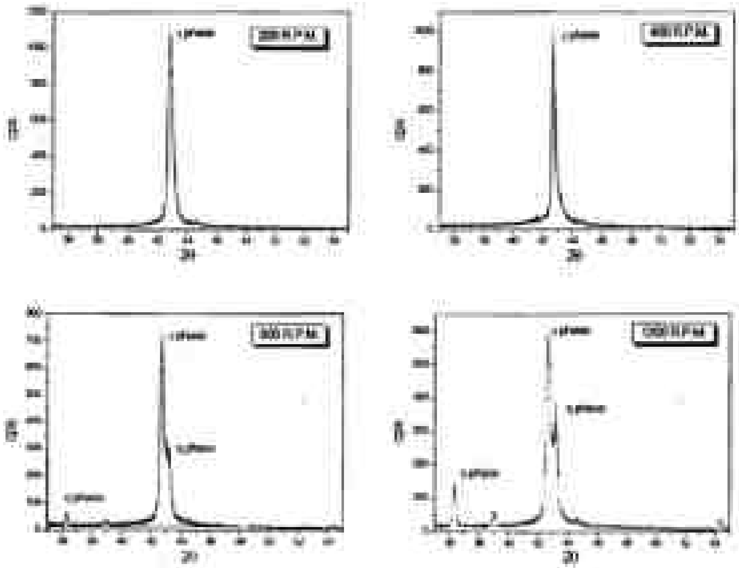

Fig. 9—X-ray diffraction patterns of the Zn-Ni alloy deposits at different rotation speeds.

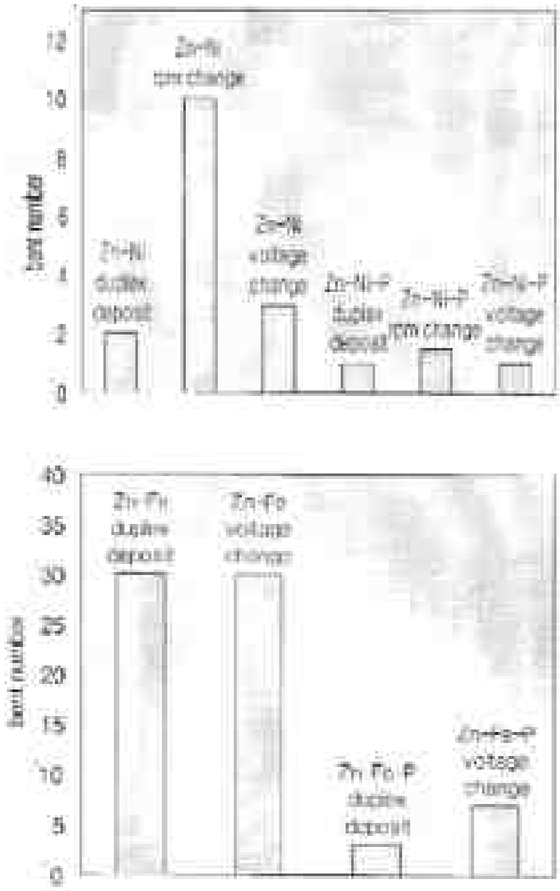

Fig. 10—Adhesion test results for gradient alloy and conventional duplex alloy deposits.

Adhesion Tests

Adhesion test specimens were prepared by preparing 25-µm thick zinc-based alloy deposits on 1-mm thick steel coupons, measuring 7 mm x 25 mm. Plating was carried out at 60ºC, with voltages ranging from 2.29 to 2.90 V (vs. SCE) for Zn-Ni and 1.10 to 2.15 V for the other alloys. Rotation speed ranged from 200 to 1200 RPM. The coupons were fixed in a bend tester (Φ = 4 mm) and folded 180º (KSD0254). Adhesion is expressed as the number of reciprocal bends endured without blistering. The results are shown in Fig. 10. All gradient alloy deposits showed superior adhesion results when compared with conventional duplex alloys.

Corrosion Tests

A five-percent NaCl neutral salt spray test (KSD9502) was performed on 25-µm thick deposits of the four gradient alloys at 35ºC for 72 hr. Rating values between 9.8-1 and 9.8-2 (KSD9502) were found. These results show good corrosion resistance.

Conclusions

Gradient electrodeposits of Zn-Ni, Zn-Fe, Zn-Ni-P and Zn-Fe-P were made by varying the speed of a rotating disc and the applied plating voltage. The corrosion resistance and adhesion of all gradient alloy coatings were better than those of conventional duplex coatings.

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