# **Electrodeposition of Zinc-Manganese on Steel Strip**

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Zinc with about 40 percent manganese was deposited at a cathode current efficiency of 60 percent in a sulfate/citrate bath with a flow rate of 2 m/see. A small amount (0.1 5 g/L) of sodium thiosulfate was added to maximize efficiency. Coatings with a consistent, desired

composition were produced using a conventional, horizontal electrogalvanizing line equipped with nozzles for uniform solution flow.

teel plated with zinc alloys provides good cormechanical properties.<sup>14</sup> Zinc-iron and zincnickel are two of the alloys that have been used extensively by Japanese automakers demanding coatings with exceptional corrosion resistance.<sup>74</sup>

Another alloy that has shown promise is zinc-manganese. The codeposition of manganese from a sulfate/ citrate bath<sup>10</sup> also affords the excellent corrosion protection, paintability, and other properties desired by automobile manufacturers. " A viable process that produces a zinc alloy containing approximately 40 percent manganese has been developed.

# **Experimental Procedure**

The sulfate/citrate bath contained zinc sulfate, manganese sulfate, and sodium citrate, which acts as a completing agent (Table 1). In some experiments, the bath composition



Fig. 1-Flow cell.

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and pH were varied; pH was adjusted using sodium hydroxide or sulfuric acid.

Electrodeposition was conducted under potentiostatic or galvanostatic conditions using a flow cell with a steel cathode and a parallel Pt-coated titanium anode (Fig. 1). During potentiostatic electrolysis, the potential was measured through a capillary, which was inserted from the back of the cathode to the cell. To avoid disturbing electrolyte flow, the top of the capillary was set at the level teel plated with zinc alloys provides good cor- of the cathode surface. The reference electrode was rosion resistance, weldability, paintability, and Ag/AgCl.





Fig. 2—Effect of current density and flow rate on Mn content of deposit.

Fig. 3-Effect of temperature on Mn content of deposit.

The deposit obtained was dissolved in dilute hydrochloric acid. The dissolved zinc and manganese were analyzed by atomic absorption spectrometry to determine the alloy composition and cathode current efficiency. To maintain the bath, the reduction of oxidized manganese ions was monitored. Bath stability was evaluated by measuring the precipitates that formed after storage for 20 days at 50° C. Trivalent manganese was reduced to Mn<sup>2+</sup>ions using pieces of zinc and manganese. The absorbance of the bath was measured to determine whether or not reduction had occurred.

Zinc-manganese alloys were electrodeposited on steel strip in a horizontal electrogalvanizing line using plating cells equipped with electrolyte-injecting, slit-type nozzles.<sup>12</sup> The uniformity of the alloy deposits was determined by examining the distribution of zinc and manganese in the depth direction of the coatings by glow-discharge spectrometry.

# **Alloy Composition**

The effect of current density and flow rate on the composition of Zn-Mn alloys deposited from the standard bath is shown in Fig. 2. Only zinc, which is electrochemically more noble than manganese, was deposited in the low-current-density range (<10 A/dm<sup>2</sup>). The two metals were codeposited at a higher current density. The content of manganese, which is less noble than zinc, increased with increasing current density. Manganese peaked at 30 or 40 A/dm<sup>2</sup> and decreased with further increases in current density. In this current density range, the deposit was burned.

An increase in flow rate extended the current density range to a point at which only zinc was deposited, and decreased the Mn content when current density was fixed. Furthermore, an increase in flow rate shifted the current density at which the Mn content peaked.

The effect of temperature on the composition of alloys electrodeposited from the standard bath is shown in Fig. 3. Raising the temperature had about the same effect as increasing the flow rate.

Figure 4 shows the effect of pH on the Mn content of the coating deposited from the standard bath. The Mn content declined with a decrease in PH.



Fig. 4-Effect of pH on Mn content of deposit.

The relationship between the Mn content of the deposit and the metal percentage of Mn in the bath  $(Mn^{2+}/Zn^{2+} + Mn^{2+})$  by wt) is shown in Fig. 5. The total metal ion concentration was kept constant at 0.42M. The percentage of Mn in the deposit increased directly with the metal percentage of Mn in the bath, but the increase depended on current density. The effect of the sodium citrate concentration is shown in Fig. 6. A decrease in sodium citrate reduced the Mn content of the deposit.

As mentioned earlier, the composition of electrodeposited Zn-Mn alloys varied considerably with a change in plating variables. The effects of these variables on partial cathodic polarization curves were investigated. Figure 7 shows partial cathodic polarization curves for Zn-Mn alloy







Fig. 6—Effect of sodium citrate concentration of bath on Mn content of deposit.

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electrodeposition from the standard bath at 50° C with a flow rate of 2 m/see. Figure 8 represents the effect of flow rate and temperature on partial cathodic polarization curves.

The amount of Zn and Mn in the deposits was determined by atomic absorption spectrometry. Once these data were collected, the partial current densities (i) of Zn and Mn were calculated:

$$i_{Zn} = \frac{W_{Zn}}{m_{Zn}/2} \cdot \frac{96,500}{t}$$
$$i_{Mn} = \frac{W_{Mn}}{m_{Mn}/2} \cdot \frac{96,500}{t}$$



Fig. 7—Partial cathodic polarization curves for deposition of Zn-Mn alloy.

$$\mathbf{i}_{\mathbf{H}_{2}} = \left[ \frac{\mathbf{Q}}{\mathbf{A}} - \mathbf{i}_{\mathbf{Z}\mathbf{n}} \cdot \mathbf{t} - \mathbf{i}_{\mathbf{M}\mathbf{n}} \cdot \mathbf{t} \right] / \mathbf{t}$$

where  $W_{zn}$  is the weight of Zn in the deposit in g/dm<sup>2</sup>,  $W_{M_n}$  is the weight of Mn in the deposit in g/dm<sup>2</sup>,  $m_{zn}$ . is the atomic weight of Zn (65.37), $m_{M_n}$  is the atomic weight of Mn (54.94), Q is the quantity of electricity (c) applied (Q = 270c at -1400 mV or less and 40 or 135 c at -1300 mV or a more noble potential), t is the electrolysis time in see, and A is the area of deposition in dm<sup>2</sup> (A= 0.17 dm<sup>2</sup>).

Even at a potential range less noble than that in which the limiting current density was reached, the partial current density of zinc varied with the potential. However, the partial current density was relatively high at a high flow rate and temperature. This indicates that the partial current density of zinc is controlled by diffusion. Elevating the temperature increases the diffusion constant of zinc and zinc-citrate complex ions and the zinc ion concentration due to a decrease in the formation constant of zinc-citrate complex ions.

The slight increase in the partial current density of zinc at -1700 to-1900 mV maybe the result of agitation caused by an increase in hydrogen evolution. The decrease in the partial current density of zinc in the less-noble potential range may be related to an increase in pH in the vicinity of the cathode due to abundant hydrogen evolution, which promotes the formation of zinc-citrate complex ions, thus suppressing zinc deposition.

Manganese began to be deposited at -1500 to -1600 mV. The partial current density of Mn approached the limiting current density with high polarization and decreased at a potential range less than that of the limiting current density, where the deposit was burned. An increase in the flow rate raised the limiting current density. However, the partial polarization curve of Mn was only slightly changed by flowrate changes except in the range producing burnt deposits. Temperature increases also had only a slight effect on the partial cathodic polarization curve of Mn. These results indicate that the deposition rate of Mn is not diffusion controlled in the region in which useful Zn-Mn alloys are deposited.



Fig. 8—Effect of flow rate and temperature on partial cathodic polarization curves of (a) zinc, (b) manganese, and (c) hydrogen for deposition of Zn-Mn oys.

The partial current density of hydrogen was affected by diffusion at a potential more noble than -1700 mV, but only slightly so at a less noble range. The slope of the partial polarization curve for hydrogen changed sharply at -1700 to -2100 mV (Fig. 8c), demonstrating that hydrogen evolution was promoted.

Only zinc was deposited at -1100 to-1500 mV (Figs. 7 and 8). When manganese began to be codeposited with zinc, the partial current density of Mn increased sharply toward the less noble direction, whereas the partial current density of Zn decreased somewhat, resulting in an increase in the Mn content of the alloy. An increase in flow rate and temperature increased the partial current density of zinc (due to the promotion of diffusion) but did not affect that of Mn. The Mn content of the deposit decreased with increasing flow rate and/or temperature.

The deposition potential of Zn shifted to the noble direction and its partial current density increased when the solution pH was reduced from 5.6 to 5.0 (Fig. 9). On the other hand, the deposition potential of Mn became less noble. These observations indicate that: (1) the zinc-citrate ion formation was reduced by the pH decrease, which increased the uncompleted Zn ion concentration and thereby increased the limiting current density of Zn, and (2) the formation of manganese-citrate complex ions was increased by the decrease in PH. The net result was promotion of Zn and suppression of Mn deposition. A decrease in the concentration of sodium citrate may decrease the formation of zinc-citrate complex ions, thus increasing the partial current density of zinc and its deposition rate.

#### **Cathode Current Efficiency**

The cathode current efficiency decreased as the manganese content of the deposit increased (Fig. 10). Cathode current efficiency is expressed as follows:



Fig. 9—Effect of pH on partial cathodic polarization curves for deposition of Zn-Mn allovs.

$$\begin{aligned} & = (\mathbf{i}_{Zn} + \mathbf{i}_{Mn})/(\mathbf{i}_{Zn} + \mathbf{i}_{Mn} + \mathbf{i}_{H_2}) \\ & = (1 + \mathbf{i}_{Mn}/\mathbf{i}_{Zn})/(1 + \mathbf{i}_{Mn}/\mathbf{i}_{Zn} + \mathbf{i}_{H_2}/\mathbf{i}_{Zn}) \\ & = (1 + \mathbf{i}_{Zn}/\mathbf{i}_{Mn})/(1 + \mathbf{i}_{Zn}/\mathbf{i}_{Mn} + \mathbf{i}_{H_2}/\mathbf{i}_{Mn}) \end{aligned}$$

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where  $i_{Zn}$ ,  $i_{Mn}$ , and  $i_{H_2}$  represent the partial current densities of zinc, manganese, and hydrogen, respectively. This equation demonstrates that the cathode current efficiency is determined only by the Mn content if  $i_{H_2}/i_{Zn}$  or  $i_{H_2}/i_{Mn}$  is constant;  $i_{H_2}/i_{Zn}$  is not constant in the potential range in which zinc and manganese are codeposited (Fig. 7). By contrast,  $i_{H_2}/i_{Mn}$  is nearly constant, as shown in Fig. 11, where data for deposits containing more than 10 percent by wt Mn are plotted. Because  $i_{H_2}$  and  $i_{Mn}$  are nearly



Fig. 10—Relationship between cathode current efficiency and Mn content cl deposit.



Fig. 11—Relationship between partial current densities of hydrogen end manganese.

independent of flow rate and temperature in the range of codeposition (Fig. 8), it is understood that  $i_{\rm HZ}/i_{\rm Mo}$  is not affected by flow rate and temperature.

The effect of pH on cathode current efficiency is shown in Fig. 12. Using the standard bath, the cathode current efficiency was not affected by pH 5.0 to 5.6. However, the cathode current efficiency decreased at pH values lower than 4.5.

Although the standard bath (Table 1) has a high cathode efficiency, this value is reduced as the manganese concentration is increased. Therefore, additives for increasing efficiency were investigated. Adding small amounts of sulfur compounds such as sodium thiosulfate, telluric acid, and selenic acid markedly increased efficiency. Sodium thiosulfate proved to be the best because it did not adversely affect corrosion resistance or paint adhesion as did the other additives.

Figure 13 shows the effect of sodium thiosulfate on cathode efficiency, which was increased from about 40 to 60 percent for alloys containing approximately 40 percent Mn. Although adding 0.1 or 0.15 percent sodium thiosulfate improved efficiency, the reason for this improvement has not been clarified.

# **Bath Stabilization**

A previous report'" indicated that precipitation occurred in a sulfate/citrate bath. In the study reported here, no precipitates formed when the bath was stored at 50° C for 20 days at pH 5.4 to 6.0. However, Fig. 14 shows that precipitate formation did occur at pH 3.0 to 5.4.

Divalent manganese ions are oxidized by dissolved oxygen or oxidation reactions on insoluble anodes. An increase in the concentration of oxidized Mn ions reduced the cathode current efficiency. To avoid this, metal pieces were used to reduce oxidized manganese ions to Mn<sup>2+</sup> ions. Figure 15 shows absorbance of the bath before deposition, after plating using a platinum-coated titanium anode, and after reaction with metallic zinc.



Fig. 12-Effect of pH on cathode current efficiency.



Fig. 12-Effect of sodium thiosulfate additions on cathode current efficiency.







Fig. 15—Absorbance of bath (a) before plating, (b) after plating using 1.7 Faraday/L, and (c) after reaction with metallic zinc.

After plating, a strong absorbance peak appeared at approximately 430 nm. However, the peak disappeared after the bath reacted with metallic zinc. The peak at 430 nm was believed to be characteristic of Mn<sup>3+</sup>-citrate complex ions. Accordingly, the results described previously show that Mn<sup>3+</sup>ions were generated during plating but were reduced to Mn<sup>2+</sup>ions on the surface of metallic zinc. Trivalent Mn ions were also reduced on the surface of metallic manganese. Thus, oxidized Mn ions can be reduced by reaction with either zinc or manganese.

### **Manufacturing Process**

Steel plated with Zn-Mn alloys can be produced on a conventional electrogalvanizing line using zinc and insoluble anodes and simultaneously supplying Mn ions to the bath by dissolving metallic manganese. However, plating variables must be strictly controlled to produce uniform Zn-Mn deposits. Alloy composition is sensitive to operating variables, especially to electrolyte flow in the plating cell. The flow should be uniform but is often undermined by the apparatus used for agitation.

To determine whether or not uniform deposits could be produced on an industrial scale, Zn-Mn alloys were plated on steel strip on a horizontal electrogalvanizing line equipped with slit-type, electrolyte-injecting nozzles. A depth profile (Fig. 16) analyzed by glow-discharge spectrometry showed that uniform alloy coatings were indeed produced.

## Summary

The deposition potentials of zinc and manganese deposited from a sulfate/citrate bath at a high solution flow rate differed considerably. Codeposition of Zn and Mn occurred only at relatively high current density. The manganese content increased with increasing current density.

The deposition rate of zinc increased with increasing



Fig. 16—Depth profile of deposit analyzed by glow-discharge spectrometry.

flow rate and/or temperature, both of which promote diffusion, while that of manganese was not diffusion controlled. The pH affected complex ion formation and deposit composition. A pH of 5.4 to 6.0 prevented the formation of precipitates. Adding 0.1 or 0.15 g/L sodium thiosulfate improved cathode current efficiency. A uniform deposit was obtained on steel strip in a horizontal plating line equipped with nozzles for uniform solution flow.

#### References

- 1. T. Watanabe et al., SAE Tech. Paper 820,424 (1982).
- 2. N. Miura et al., Trans. ISIJ, 23, 11,913 (1983).
- 3. A. Shibuya et al., ibid., 23, 11,923 (1983).
- 4. T. Adaniya et al., Plat. and Surf. Fin., 72,52 (Aug. 1985).
- 5. W.R. Johnson and J.B. Vrable, SAE Tech. Paper 840,213 (1 984).
- 6. M.R. Lambert and R.G. Hart, SAE Tech. Paper 860,266 (1 986).
- 7. M. Nabatame et al., Nippon Kokan Overseas Tech. Report 40, p. 9 (1984).
- 8. A. Komoda et al., AES 4th Continuous Strip Plating Symp., Chicago (May 1984).
- 9. R. Noumi et al., ibid.
- 10. A. Brenner, Electrodeposition of Alloys, Vol. 2, Academic Press, New York, NY, 1963; p. 152.
- 11. M. Sagiyama et al., SAE Tech. Paper 860,268 (1986).
- 12. M. Kawabe et al., Trans. ISIJ, 25, B-260 (1985).







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