### Morphology and Composition of Electrodeposited Zinc-Manganese Alloys

By M. Eyraud, A. Garnier, F. Mazeron and J. Crousier

The influence of plating conditions on the morphology and composition of electrodeposited Zn-Mn alloys was studied. The manganese content depends on the composition, the pH, the temperature and the stirring of the bath. It also depends on the current density used to prepare the deposits. The morphology was observed by scanning electron microscopy, and the manganese content was determined by energy dispersive X-ray analysis. The structure was determined by X-ray diffraction. A 12 a/o (atomic percent) Mn alloy was compared with an alloy of the same composition prepared by melting. They showed the same diffractogram.

The literature contains few results on electrocrystallization of zinc-manganese alloys. The findings lack precision and are even contradictory. The only common parameter is the components of the baths, which are ZnSO, and MnSO, in Nacitrate, as complexing agent, to bring the deposition potentials closer.<sup>1</sup> The composition of the bath varied over a large range of concentration:<sup>2-8</sup>ZnSO<sub>4</sub> from 0.03 to 0.31 M; MnSO<sub>4</sub> from 0.09 to 0.36 M; Na-citrate from 0.2 to 0.8 M. Plating was done at room temperature<sup>6</sup> or at 50 °C.<sup>2-5</sup> The pH was between 5 and 6. The manganese content of the deposit ranged from 5 to 100 a/o. Deposits containing 50 to 55 a/o Mn were obtained with current densities from 17 to 80 mA/cm<sup>2</sup> from non-stirred solutions.<sup>6</sup> Other authors, using current densities from 15 to 80 mA/cm<sup>2</sup>, claimed Mn content up to 100 a/o.<sup>8</sup> With turbulent flow, it is possible to use high current densities.<sup>2-4</sup> In this case, the Mn content increased with the applied current up to 300 mA/cm<sup>2</sup>, then at higher currents decreased and the deposits showed poor quality. The Mn content of the deposits also decreased with citrate concentration in the bath.<sup>2,3,6</sup> An increase in the Mn content of the deposit caused a decrease in the current efficiency. Addition of telluric acid or selenic acid increased the Mn content without decreasing current efficiency.<sup>2,8</sup> Influence of bath aging has also been studied.<sup>2,3,9</sup> At 50 °C, the bath precipitated 20 days later. Precipitation did not occur when bath pH was higher than 5.4. During the plating, oxidation of manganese species took place on the anode, but addition of zinc powder in the bath allowed Mn(III)-citrate to be reduced to Mn(II)-citrate.<sup>2,4</sup>

The goal of this study was to prepare Zn-Mn deposits from the citrate bath described in the literature, and to test whether it is possible to use this type of bath to prepare coatings. This study describes the morphology and the composition of Zn-Mn alloys obtained by changing the composition, pH and temperature of the bath, and the applied current density.

#### **Experimental Procedure**

#### Deposit Preparation

Electrocrystallization of Zn-Mn binary alloys was conducted on cold-rolled low-carbon steel strip (0.28% Mn) substrates, having an active surface area of 4.5 cm<sup>2</sup>. The counterelectrode was a gold sheet and all the potentials were reported with respect to a saturated calomel electrode. The pretreatment procedure applied to the steel strips before each deposition consisted of the following sequence:

(1) cleaning of the surface with trichloroethylene, and rinsing with water; (2) immersing the sample in a 30-percent hydrochloric acid bath for 5 min and rinsing with water; (3) polishing on automatic apparatus with emery paper down to 1200 grit; (4) cleaning in an ultrasonic bath.

Steps (3) and (4) were performed just before the electrocrystallization experiments.

Plating baths were composed of  $ZnSO_4$ ,  $MnSO_4$  and sodium citrate. To study a large range of bath compositions and pH, several solutions were prepared in which zinc content remained constant (0.24 M) and the manganese content was varied from 0.12 M to 0.50 M. Bath formulations are indicated before the corresponding experiments. The apparatus consisted of a potentiostat/galvanostat<sup>a</sup> (Par 273) and a microcomputer system.



Fig. 1—Morphology of deposit from 0.12M  $MnSO_4$ . Current density, 20 mA/cm<sup>2</sup>.



Fig. 2—Current efficiency vs. current density for freshly prepared solution and after two months' aging.



Fig. 3—Manganese content vs. current density for freshly prepared solution and after two months' aging.



Fig. 4—Manganese in deposit: 30 a/o; 0.30 M MnSO<sub>4</sub> solution; current density, 25 mA/cm<sup>2</sup>.



Fig. 5—Manganese in deposit: 35 a/o; 0.30 M MnSO<sub>4</sub> solution; current density, 35 mA/cm<sup>2</sup>.



Fig. 6—Cross section of  $10-\mu$ m-thick deposit from 0.30 M MnSO<sub>4</sub> solution; current density, 15 ma/CM<sup>2</sup>.

#### Coating Analysis and Characterization

Surface morphology was examined by optical and scanning electron microscopes (SEM). Chemical analysis of the surface was performed by energy dispersive X-ray analysis (EDAX). To verify the validity of the results obtained by EDAX, some analyses were performed by atomic absorption spectroscopy (AAS) after dissolving the coatings. The table shows a comparison of the a/o Mn obtained by the two methods for five samples prepared under the same experimental conditions. The results are similar and, because EDAX is easier and faster than atomic adsorption analysis, all compositions were determined by EDAX.

The thickness of the deposits was estimated by weighing the steel strips before and after coating. Comparison with the thickness, determined by Faraday's law from the charge provided, made it possible to determine current efficiency. Structural analyses were performed using an X-ray diffractometer.<sup>b</sup> (D 5000 Siemens)

#### Results

## From a Bath Containing 0.24 M ZnSO $_4$ , 0.12 M MnSO $_4$ and 0.61 M Mn-citrate, pH 6.1

Deposits were made galvanostatically for currents from 20 to 40 mA/cm<sup>2</sup>, and potentiostatically at -1800 mV. The bath was stirred or not stirred; the temperature was from room temperature to 50 °C. Whatever the deposition conditions, deposits analyzed by EDAX showed no manganese content. Analyses performed by AAS gave 0.28 percent Mn, which is, as indicated earlier, the manganese content of the steel substrate. For the smallest currents, the morphology of the coatings took the form of hexagonal plates, characteristic of a pure zinc deposit (Fig. 1). For the highest currents, dendrites were observed above the plates.

From a Bath Richer in Manganese (0.30 M MnSO,) As will be seen later, this bath made it possible to obtain deposits containing a noticeable percentage of manganese. The bath was first tested for its stability. Two series of tests were conducted under currents from 15 to 50 mA/cm<sup>2</sup>. The first series (1) was performed with the freshly prepared bath and the second series (2) after two months' aging. The results are reported in Fig. 2, which shows current efficiency as a function of current density, j, and in Fig. 3, which shows manganese content as a function of *j*. The current efficiency decreases with the applied current density; also with solution aging. On the other hand, the manganese content increases with j and with bath aging. The applied current was divided among three reactions: Reduction of zinc and manganese cations, and hydrogen evolution;  $j_{appl} = j_{H2} + j_{Mn} + j_{Zn}$ . The kinetics of hydrogen evolution was determined on bulk manganese and zinc in sodium citrate solution without reducible cations. For a potential of 1.8 V, the current density was 5 mA/cm<sup>2</sup> for zinc and 42 mA/cm<sup>2</sup> for manganese. These values indicate that the presence of manganese increased the part of the current consumed by hydrogen evolution; this, therefore, explains the decrease in current efficiency. Some authors have indicated that the pH of the solution is a parameter of first importance for bath aging.<sup>2</sup> Addition of zinc powder in the solution may also slow the aging. An industrial bath should therefore test zinc and manganese anode efficiency.

<sup>a</sup> Model 273, EG&G Princeton Applied Research, Princeton, NJ <sup>b</sup> Model D 5000, Siemens, Germany



Fig. 7—Lower part of steel substrate; 0.30 M  $MnSO_{a'}$  current density, 35 mA/cm<sup>2</sup>.



Fig. 8—Upper part of steel substrate; 0.30 M MnSO<sub>4</sub>, current density, 35 mA/cm<sup>2</sup>.



Fig. 9—Current efficiency vs. current density for stirred and unstirred baths.







Fig. 10—Manganese content vs. current density for stirred and unstirred baths.

Fig. 11—Current efficiency vs. current density for various values of pH.

Fig. 12—Manganese content vs. current density for various values of pH.

As seen in Fig. 3, the manganese content in deposits varied from 23 to 46 a/o. Manganese in the deposit can be detected by optical microscope, because as soon as a very low percentage of manganese is present in the deposit, the hexagonal plate structure characteristic of pure zinc deposits disappears and the morphology becomes nodular (Figs. 4 and 5). The size of the nodules decreased when the applied current increased. Because of low current efficiency, the deposits were thin:  $3 \mu m$  for  $j = 25 \text{ mA/cm}^2$  (the deposit in Fig. 4) and 2.5  $\mu$ m for j = 35 mA/cm<sup>2</sup> (the deposit in Fig. 5). A thicker deposit (10  $\mu$ m) was made with 15 mA/cm<sup>2</sup>. The cross section (Fig. 6) shows a structure composed of two layers; the layer of about 4  $\mu$ m near the substrate was porous and the top 3- $\mu$ m layer was compact. The X-ray map shows good distribution for manganese and zinc and no variation of the manganese and zinc content through the two layers. The bath containing 0.3 M MnSO<sub>4</sub> made it possible to obtain a significant amount of manganese in the deposit. Accordingly, this bath was used to study the influence of the various plating parameters on the characteristics of the deposits.

#### Influence of the Different Stages Of Bath Preparation

Because the cations are not free but complexed, it appears possible to observe a competition between the species to be complexed. The preceding bath (0.30 M MnSO<sub>4</sub>) was prepared in the following stages:

1. Preparation of the MnSO<sub>4</sub> solution;

2. Addition of ZnSO<sub>4</sub>;

3. Addition of Na citrate.

Some authors used the following stages:<sup>6</sup>

- 1. Preparation of separate solutions of ZnSO<sub>4</sub>, MnSO<sub>4</sub> and Na-citrate;
- 2. Mixing of zinc and citrate solutions;
- 3. Addition of the  $MnSO_4$  solution 8 hr later.

A bath with the same composition as the bath above (0.30 M  $MnSO_4$ ) was prepared using this last sequence. Whatever the current, with or without stirring, the deposit contained no manganese. This experiment shows that the sequence of the stages is of first importance. Therefore, the baths used to study the influence of the other parameters were prepared using the first sequence.

#### Influence of Stirring

An experiment was performed using a bath stirred with a magnet, at 35 mA/cm<sup>2</sup>. The substrate was immersed vertically in the bath, and the part near the stirring magnet was coated with a deposited layer thicker than that obtained on the upper part. The micrograph in Fig. 7, which illustrates the lower part, shows irregular nodules larger than the ones obtained from a non-stirred solution. The micrograph in Fig. 8 shows the smaller and regular nodules obtained on the upper part. EDAX of the coating shows that the thicker deposit is less rich in Mn (10%) than the deposit on the upper part (21%).

Figures 9 and 10 show the relation between the applied current and the current efficiency and the Mn content, respectively, for stirred and non-stirred baths. Stirring increased the current efficiency and decreased the Mn content. That is in accordance with the thick manganese-poor deposit obtained on the lower part of the substrate.



Fig. 13—Current efficiency vs. current density for various concentrations of Mn.



Fig. 14—Manganese content vs. current density for various concentrations of Mn.



Fig. 15—Cross section of a deposit from 0.30 M  $MnSO_4$  at 30 mA/cm<sup>2</sup>.



Fig. 17—Current efficiency vs. current density at 25 and 50 °C.

Fig. 18-Manganese content vs. current density at 25 and 50 °C.

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#### Effect of pH

MnSO<sub>4</sub> at 20 mA/cm<sup>2</sup>.

To study a large variation of pH, two baths were prepared at pH 3 and 9. The solutions precipitated after 12 hr; the acid bath as pink species covering the walls of the cell, which may be Mn-citrate;<sup>9</sup> the alkaline bath as dark brown species, which may be manganese dioxide. This result is of concern because it indicates that the pH range that can be used is very narrow. The effect of pH was therefore studied between 5.7 and 6.3. The results obtained for currents from 15 to 60 mA/ cm<sup>2</sup> are shown in Figs. 11 and 12. The graphs show that the pH is of first importance, and show the strong effect of variations of about 0.2 pH unit. The current efficiency decreased when the applied current increased and when the pH increased. The graph in Fig. 12 shows that high pH increased the Mn content.

#### Influence of Higher Mn Content

Baths containing the same amount of ZnSO<sub>4</sub> and MnSO<sub>4</sub> from 0.30 to 0.50 M, were prepared. The results are reported in Figs. 13 and 14. The bath containing 0.50 M MnSO<sub>4</sub> possessed very low current efficiency (2 %), but the Mn content was about 94 a/o. For currents higher than 25 mA, a steep increase in manganese content was observed (Fig. 14). For this solution, containing the largest amount of manganese (0.5 M), manganese content in the deposit increased sharply for current densities from 30 mA upward, but concomitantly, the current efficiencies were very low.

electrodeposited Zn-Mn + JCPDS data for pure Zn 322 а Counts electrodeposited Zn-Mn + JCPDS data for β Zn 322 b Counts ۰. **2**0

Fig. 19—Diffractogram patterns for electrodeposited Zn-Mn alloy: (a) pure Zn; (b) Mn.

Figures 15 and 16 show cross sections of two deposits obtained from the 0.30 M Mn bath at 30 mA/cm<sup>2</sup> and from the 0.35 M bath at 20 mA/cm<sup>2</sup>. Their thicknesses were 12 and 11 um, respectively. The deposit illustrated in the micrograph of Fig. 15 is columnar, consequently porous, with Mn content of 30 a/o. This deposit can be compared with the deposit in Fig. 6, prepared from the same bath, but with a larger current. The deposit in Fig. 16 is smooth and compact and contains 27 a/o Mn, which is very close to the manganese content of the other deposit. The current efficiencies were also similar. Comparison of the two deposits shows that the structure was determined not only by the amount of manganese in the bath, but also by the current density.

#### Influence of Bath Temperature

The results from the solution containing 0.30 M MnSO<sub>4</sub> are shown in Figs. 17 and 18. The current efficiency increased with temperature, but the manganese content decreased. The increase in temperature resulted in increase of the limiting current and allowed well-crystallized deposits to be obtained for currents that gave powdered deposits at room temperature.

#### X-ray Diffraction

When an alloy has been obtained by electrocrystallization, a question arises; is the deposit an alloy (mono or polyphased) or the juxtaposition of pure zinc and manganese crystallites?

To answer this important question, Xray diffraction analysis was conducted on an electrodeposited Zn-Mn alloy. For comparison, the analysis was also conducted on a Zn-Mn alloy prepared by melting pure zinc and manganese to obtain a bulk alloy with similar composition. In both cases, the manganese content was determined by AAS and was 12 a/o manganese. Figure 19 shows the diffractogram of electrodeposited Zn-Mn. The pattern for pure zinc (Fig. 19a) and that for pure manganese (Fig. 19b) were superimposed. Comparison shows that the deposit does not contain a pure zinc or manganese phase, except perhaps a  $\beta$ Mn phase. The equilibrium phase diagram<sup>10</sup> indicates a Zn<sub>88</sub>Mn<sub>12</sub> compound at the  $\delta_1$  phase boundary; therefore, two possibilities exist: a biphase compound,  $\delta_1 + \gamma_1$ , having a

low  $\gamma_1$  phase content, or only a  $\delta_1$  phase. It is likely that the alloy corresponds to the  $\delta_1$  phase. Inasmuch as there is no Zn-Mn pattern available in the JCPDS (Joint Committee on Powder Diffraction Standards) file, various structures were simulated and the best fit was obtained for Zn<sub>7</sub>Fe, which is isostructural to the  $\delta_1$  phase of the Zn<sub>88</sub>Mn<sub>12</sub> compound.<sup>10</sup> Figure 20 shows the comparison with the pattern for Zn<sub>2</sub>Fe. The shift of the rays is a result of the difference of the lattice constants. Variations in the relative heights of the diffraction peaks suggest preferential orientations of the growing crystallites. Figure 21 is a comparison between electrodeposited and bulk Zn-Mn alloy spectra. The spectra are similar, except for some rays in the powder spectra that could not be identified. The pattern for Zn<sub>2</sub>Fe is also superimposed.

#### Conclusions

From the 0.24 MZnSO<sub>4</sub>, 0.18MMnSO<sub>4</sub> solution, whatever the current density, the pH, the temperature, and the stirring, the deposits contained no manganese. Baths containing  $0.30 \,\mathrm{M}$  (or more) MnSO, made it possible to obtain a significant manganese content in the deposits, but the current efficiency was low. Improvements in current efficiency were obtained by either stirring the bath, or decreasing the manganese content, or using baths at pH 5.7–5.9 at 50 °C. The important effect of the pH, which must be between 5.7 and 6.3, rules out the use of this bath to prepare industrial coatings. Another difficult task is that an increase in manganese content was always obtained to the detriment of

current efficiency. In industrial plants, close control of current density on the whole substrate is not feasible; accordingly, it is impossible to obtain regular Mn content in the coating. Work is in progress to prepare Zn-Mn alloys from baths without citrate, which should not be so strongly dependent on parameter values.

X-ray analysis shows that the 12 a/o Mn deposit has the same structure as the alloy of the same composition prepared by melting. From simulation of various structures, it was shown that the 12 a/o Mn alloy is isostructural with  $Zn_7Fe$ . Experiments are in progress to study the corrosion resistance of various zinc-manganese alloys in relation to their manganese content.

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Fig. 20—Diffractogram patterns for electrodeposited Zn-Mn alloy and pure Zn<sub>2</sub>Fe.



Fig. 21—Diffractogram for Zn-Mn Alloys: (a) electrodeposited; (b) bulk.

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Eyraud

Crousier

#### About the Authors

Dr. Marielle Eyraud received her doctorate from the Université de Provence, Marseille, France. She is doing post-doctoral work in the Department of Metallurgy and Materials Engineering, Katholieke Universiteit, Leuven, Belgium.

Alain Garnier is an engineer in the Laboratoire de Physicochimie des Materiaux. He is reponsible for X-ray measurements.

Ing. Fabienne Mazeron is responsible for metallic coatings at the Direction des Etudes Techniques et Automobiles de P.S.A (Peugeot S.A.)

Dr. Jacqueline Crousier is a professor at the Laboratoire de Physico-chimie des Matériaux, Université de Provence, 3, Place Victor Hugo, 1331 Marseille Cedex 3, France. Her main research activities are in electrocrystallization, corrosion and electrocatalysis for hydrogen evolution.

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