Electrodeposition of Zinc-iron alloy

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To protect steel against environmental attack, zinc-iron alloy deposition is used. Search for a non-cyanide plating bath resulted in the development of sulphate bath. Current efficiency, throwing power and Hull cell studies were used to optimise a plating bath. The optimized plating bath composition is zinc sulphate 0.05M, ferrous ammonium sulphate 0.01M, sodium sulphate 20 g L\(^{-1}\), boric acid 30 g L\(^{-1}\), methanol 0.12M, triethanolamine 0.2M, ascorbic acid 2.5 mM and sodium laurel sulphate 0.06M. Matte white deposits were obtained in the current density range of 2.3 A dm\(^{-2}\).

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**Keywords:** Electrodeposition, zinc-iron alloy, sulphate bath, alloy plating, triethanolamine, non-cyanide

Over two decades, zinc and electrodeposited zinc alloys achieved an important position in the protection of ferrous materials against corrosion\(^1\). Before 1990, zinc-iron alloy system was not popular outside Japan. In recent years, acidic sulphate or acidic chloride processes using citric acid became popular\(^2\). These baths were used for strip plating at 50 A dm\(^{-2}\). From alkaline non-cyanide baths zinc alloy deposits containing 0.5 to 1% iron were used. Changes in current densities changed the type of deposition. Equilibrium type codeposition was changed to anomalous type. From chloride baths, alloy composition ranging from 5 to > 75% by weight have been electrodeposited\(^3\). Iron content in deposit was raised by the addition of methanol. About 50% iron in the alloy was obtained at 4 A dm\(^{-2}\) with an efficiency of 90% \(^4\). SEM bright to bright alloys containing 0.3 to 12% iron were obtained from rack and barrel plating\(^5\). The morphologies of the deposits were influenced by the addition of cupric\(^6\) and ammonium chloride. Electrode rotation and agitation of the chloride bath influenced the morphology of the deposit\(^7\).

The present investigation deals with the development studies on the non-toxic, ecofriendly zinc-iron alloy plating bath containing triethanolamine and citrates.

**Experimental Procedure**
Copper plates (10×7.5×0.5 cm\(^2\)) were degreased with trichloromethane and kept cathodically for 2 min and then anodically for 10 s in a solution of 35 g L\(^{-1}\) NaOH + 25g L\(^{-1}\) Na\(_2\)CO\(_3\) at 30°C. These were washed in running water, followed by a dip for 10 s in 5% H\(_2\)SO\(_4\). Finally, thorough washing and drying were resorted to.

**Hull cell studies**
A Hull cell\(^11\) was employed to optimise the conditions for the production of good deposits. A cell current of 0.5 A was used for 10 min. The temperature of the cell was kept at 30 ± 1°C. Hull cell panels of copper were used. Electrolytic zinc was used as an anode.

**Current efficiency studies**
The electrodeposition assembly consisted of electrolytically pure soluble zinc anodes and copper cathodes of equal size (5x4x0.025 cm\(^3\)) immersed in a 800 mL solution in one litre wide mouthed glass vessel. Each specimen was weighed before and after plating and weight of the deposit was found from the difference. The amount of zinc in the deposit was estimated by dissolving the coating in nitric acid and titrated using EDTA method. The amount of iron was determined from the difference between alloy and zinc.

**Throwing power studies**
Haring and Blum\(^14\) cell consists of a rectangular cell with two metal cathodes measuring 9x5x0.1 cm\(^3\) filling the entire cross-section at both ends and a perforated anode of the same area. The anode was placed
between the cathodes so that its distance from one of the cathodes was 1/5 of its distance from the other.

Throwing power (%) = \( \frac{(K-C)}{(K+C-2)} \times 100 \)

where \( C \) is the metal distribution ratio between the nearer cathode and the further one. \( K \) is the ratio of the distance respectively of the further and nearer cathodes from the anode.

**Results and Discussions**

**Hull cell studies**

Various well-known addition agents and brighteners were studied in zinc sulphate 0.05 M, ferrous ammonium sulphate 0.01 M, sodium sulphate 20 g L\(^{-1}\), and boric acid 30 g L\(^{-1}\).

**Effect of methanol concentration**

Figure 1 presents the Hull cell patterns for various concentrations of methanol. In the absence of methanol, matte grey deposits were seen in the current density range up to 0.4 Adm\(^{-2}\). Semibright deposits were seen in the current density range of 0.4 Adm\(^{-2}\) to 1.55 Adm\(^{-2}\). Slate grey deposits were seen in the current density range of 1.55 Adm\(^{-2}\). Introduction of methanol (0.12M) modified the pattern. Matte grey deposits were seen in the current density range up to 0.456 Adm\(^{-2}\). Bright deposits were seen in the current density range of 0.456 to 1.5 Adm\(^{-2}\). Beyond 1.5 Adm\(^{-2}\) slate grey deposits were seen. In presence of 0.36M methanol, matte grey deposits were seen in the current density range up to 0.27 Adm\(^{-2}\). Slate grey deposits were seen in the current density range of 0.27 to 0.53 Adm\(^{-2}\). Bright deposits were seen in the current density range of 0.5 to 0.95 Adm\(^{-2}\). Matte grey deposits were seen in the current density range of 0.95 to 2.1 Adm\(^{-2}\). Beyond 2.1 Adm\(^{-2}\), dark grey deposits were seen. In presence of 0.48M methanol, matte grey deposits were seen in the current density range of 0.1 to 0.9 Adm\(^{-2}\). In the current density range of 0.9 to 1.9 Adm\(^{-2}\), slate grey deposits were seen. Beyond 1.9 Adm\(^{-2}\) dark grey deposits were seen.

**Effect of triethanolamine (TEA) concentration**

Figure 2 presents Hull cell patterns for various concentrations of TEA. In presence of 0.025M TEA, matte grey deposits were seen in the current density range of 0.26 Adm\(^{-2}\). Semi bright deposits were seen in
the current density range of 0.51 to 1.55 Adm\(^{-2}\). Beyond 1.55 Adm\(^{-2}\) slate grey deposits were found. Increase of TEA concentration to 0.1 M resulted in light grey matte deposits in the current density range of 0.05 to 0.32 Adm\(^{-2}\). Semi bright milky deposits were seen in the current density range of 0.32 to 1.46 Adm\(^{-2}\). Slate grey deposits were seen in the current density range of 1.46 to 3.1 Adm\(^{-2}\). In presence of 0.2 M TEA, matte grey streaky deposits were seen in the current density range of 0.1 to 1.76 Adm\(^{-2}\); slate grey deposits were seen in the current density range of 1.76 to 3.1 Adm\(^{-2}\). At extreme higher current densities dark grey deposits poorly covering the surface were seen. In 0.4 M TEA solutions, matte grey deposits were seen in the current density range of 0.05 to 0.18 Adm\(^{-2}\). Semi bright deposits were seen in the current density range of 0.18 to 1.3 Adm\(^{-2}\). Beyond 1.3 Adm\(^{-2}\), slate grey deposits were seen.

**Effect of ascorbic acid concentration**

Introduction of 0.0025 M ascorbic acid modified the Hull cell patterns (Fig. 3). In the low current density region upto 0.3 Adm\(^{-2}\) matte grey deposits were seen. Bright deposit was seen in the current density range of 0.3 to 1.0 Adm\(^{-2}\). From 1.0 to 3.1 Adm\(^{-2}\) slate grey deposits were seen. When the concentration of ascorbic acid was increased to 0.0075 M, the current density for bright deposit was reduced while the slate grey deposit was obtained in the current density range of 0.74 to 3.1 Adm\(^{-2}\). In presence of 0.01 M concentration, upto 0.05 Adm\(^{-2}\) no deposit was seen. Matte grey deposits were observed in the current density range of 0.05 to 0.67 Adm\(^{-2}\) followed by slate grey deposits at higher current densities.

**Effect of sodium lauryl sulphate (SLS) concentration**

Introduction of SLS drastically modified the patterns (Fig. 4). In presence of 0.02 M SLS, matte white deposits were obtained in the low current density range upto 0.2 Adm\(^{-2}\). Matte grey with streaky deposit was seen in the current density range of 0.2 to 0.53 Adm\(^{-2}\). Slate grey deposits were seen in the current density range of 0.53 to 3.1 Adm\(^{-2}\). When the concentration of SLS was raised to 0.06 M, the current density range for matte grey deposit widened. Bright deposits were seen in the current density range of 0.3 to 1.03 Adm\(^{-2}\). Slate grey deposits were seen in the current density range of 1.03 to 2.25 Adm\(^{-2}\). Dark grey deposits were obtained in the high current density range. When the concentration of SLS was raised to 0.08 M, the current density range for bright deposits were narrowed. Slate grey deposits were seen at current densities above 0.84 Adm\(^{-2}\).

Figure 5 presents the Hull cell pattern obtained in the optimized bath. Matte white deposit was seen in
OVERALL EFFECT

Fig. 5 — Hull cell pattern for the optimized bath.

The low current density range up to 0.24 A dm⁻². Matte grey deposits were seen in the current density range of 0.24 to 0.77 A dm⁻². At higher current densities dark grey deposits were seen.

Current efficiency

The current efficiency is given by,

\[
\% \text{Current efficiency} = \left( \frac{\text{Weight of the alloy deposited}}{\text{Theoretical weight calculated from Faraday's laws}} \right) \times 100
\]

where \( M \) is the mass of the alloy deposit; \( Q \) is the quantity of electricity passed; \( e_{\text{alloy}} \) is the electrochemical equivalent.

\[
e_{\text{alloy}} = \frac{e_{\text{Fe}} \times e_{\text{Zn}}}{e_{\text{Fe}} f_{\text{Fe}} + e_{\text{Zn}} f_{\text{Zn}}}
\]

where \( e_{\text{Fe}} \) and \( e_{\text{Zn}} \) are the electrochemical equivalents of the constituent metals; \( f_{\text{Fe}} \) and \( f_{\text{Zn}} \) are their fractions in the deposits. At each current density, the fraction of iron and zinc in the alloy deposit was used to calculate \( e_{\text{alloy}} \). The density of the alloy was calculated at each current density by taking into consideration the fraction of the constituent metal.

Figure 6 presents the variation of current efficiency with current density at pH 4. Increase of current density decreased the current efficiencies for alloy, zinc and iron up to 0.4 A dm⁻² and started increasing slightly. The current efficiencies for zinc deposition were found to be greater than that for iron.

Figure 7 presents the variation of current efficiency with pH at 0.4 A dm⁻². Increase of pH decreased the current efficiencies for alloy, zinc and iron. Increase of pH decreased the zinc content in the alloy.

Throwing power

Figure 8 presents the variation of percentage throwing power with current density. In the operating range of 2 to 2.5 A dm⁻² the bath exhibited 12 to 16% throwing power.
Table 1—Nature of the deposit with current density

<table>
<thead>
<tr>
<th>Current density Adm²</th>
<th>Nature of the deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>matte white</td>
</tr>
<tr>
<td>1.0</td>
<td>slight grey at edges and semi bright deposit in the middle</td>
</tr>
<tr>
<td>2.0</td>
<td>matte white</td>
</tr>
<tr>
<td>3.0</td>
<td>matte white</td>
</tr>
<tr>
<td>4.0</td>
<td>slight grey</td>
</tr>
<tr>
<td>5.0</td>
<td>slight grey</td>
</tr>
</tbody>
</table>

Various current densities were applied using the optimized bath. In the current density range of 2 to 3 Adm², matte white deposits were obtained. Beyond 4 Adm² slight grey deposits were seen (Table 1).

Optimized bath composition
Zinc sulphate 0.05M, ferrous ammonium sulphate 0.01M, sodium sulphate 20 gL⁻¹, boric acid 30 gL⁻¹, methanol 0.12M, triethanolamine 0.2M, sodium lauryl sulphate 0.06M, ascorbic acid 0.0025M, temperature 30°C, pH 4.

Conclusion
Zinc-iron alloy plating bath has been developed with the current efficiencies of the alloy composition of 70%. Matte white deposits were obtained in the current density range of 2 to 3 Adm².

References
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