J Solid State Electrochem (1998) 3: 48–51

SHORT COMMUNICATION

G.N.K. Ramesh Bapu · G. Devaraj · J. Ayyapparaj

Studies on non-cyanide alkaline zinc electrolytes

Received: 30 January 1998 / Accepted: 15 May 1998

Abstract An alkaline non-cyanide zinc plating solution consisting of 10 g/l zinc oxide, 90 g/l sodium hydroxide and 1.5 g/l gelatine was prepared . Using this solution, a smooth, uniform and fine-grained semi-bright deposit was obtained on mild steel sheets over a wide range of current density and pH at 303 K. The plating bath had about 63% current efficiency and 25% throwing power at 303 K and at pH 10. Caffeine and vanillin additions to this bath gave bright zinc deposits.

Key words Non-cyanide zinc · Alkaline zincate bath · Additives

Introduction

Electrodeposited zinc has been used extensively in automotive and other industrial sectors as a protective coating for large quantities of steel wires, strips, sheets, tubes and other fabricated ferrous metal parts. Zinc deposits offer good protection and decorative appeal at low cost. Since zinc is anodic to steel, it protects the basis metal even if the deposit is porous. An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency [1]. However, the critical pretreatment requirements and the poor throwing power of these solutions restrict their use to plate only on regular shaped articles. Considering pollution hazards and high industrial effluent treatment costs, non-cyanide zinc baths have been introduced in place of cyanide solutions [2]. Low toxicity, simple waste treatment, low make-up costs, good plate distribution and use of steel tanks, etc., are a few practical advantages in choosing an alkaline non-cyanide zinc bath for plating [3–6]. The effectiveness and ease of operation of these baths are totally dependent on the brightener additive systems used in the bath [7]. As most of the galvanizing industry employs proprietary baths, the details on the bath constituents, the effect of operating variables and the electrochemical characteristics of the alkaline non-cyanide zinc bath are not available.

Hence in the present investigation an attempt is being made to study systematically the bath characteristics and the effect of few organic additives. The bath solution was prepared using zinc oxide and sodium hydroxide. A Hull cell was employed to optimize the current density, pH and temperature, over which good quality deposit was obtained. The effect of caffeine and vanillin as viable brighteners for the plating solution was explored using the Hull cell. The throwing power and current efficiency of the solution were also determined at various current densities.

Experimental

Laboratory grade zinc oxide (10 g) was dissolved in 500 ml distilled water containing 90 g sodium hydroxide. About 3 g of zinc dust was added to the solution and stirred throughly. After settling, it was decanted and pre-electrolyzed at 0.3 A dm^{-2} for a day. Then it was filtered through a G-4 crucible and the filtrate was made up to 1 litre with deionized water.

Hull cell experiments

To judge the quality and nature of the zinc deposits from the zincate electrolytes at various current density, pH and temperature, plating was carried out on polished mild steel sheets using a standard 267 ml Hull cell for 5 min. The optimum concentrations of caffeine and vanillin additives were also determined using Hull cell tests at various concentrations while keeping the other parameters constant in each case.

Throwing power

A Haring-Blum cell was employed to determine the throwing power of the solution at 4 A dm^{-2}, at pH 10 and 303 K. Plating was carried out for 30 min on steel cathodes, positioned at a dis-

G.N.K. Ramesh Bapu (✉) · G. Devaraj · J. Ayyapparaj
Central Electrochemical Research Institute,
Karaikudi – 630 006 (Tamilnadu), India

tance ratio of 1:5 from the perforated zinc anode. From the weight of the deposits obtained at the near (W_n) and far cathodes (W_f), the throwing power (TP) was calculated using the Field's formula [8].

$$\text{Throwing power}(\%) = \frac{L - M}{L + M - 2} \times 100 \qquad (1)$$

where L is the linear ratio and M is the metal distribution ratio, W_n/W_f.

Current efficiency

The cathode current efficiency of the electrolyte was found at different current densities at 303 K for a duration of 1000 C. From the weight of the deposits obtained, the current efficiency was determined.

Results and discussion

Hull cell studies

Steel sheet (10.0 × 7.5 cm) and electrolytic zinc sheet was used as cathode and anode, respectively. The codes employed for recording the Hull cell patterns and the nature of the deposits at 0.5–2 A cell current are shown in Figs. 1 and 2, respectively. Below 2.5 A dm^{-2} a dull deposit was seen; between 2.5 and 5 A dm^{-2} there was a semi-bright pattern; above this limit a streaky and powdery deposit was observed. Addition of 1.5 g/l gelatine to this solution was found to reduce the powdery nature and produced a smooth, fine-grained deposit. Hence further experiments were carried out with the zincate electrolyte containing 1.5 g/l gelatine.

Keeping the temperature and cell current at 303 K and 1 A, respectively, the effect of pH was studied between 8 and 11 and the results are given in Fig. 3. At pH 8 a dull deposit was seen throughout the cathode. With an increase in pH to 9 and 10, a semi-bright deposit appeared beyond 2 A dm^{-2}. Further increase in pH gave a rough deposit with a burnt pattern above 4 A dm^{-2}.

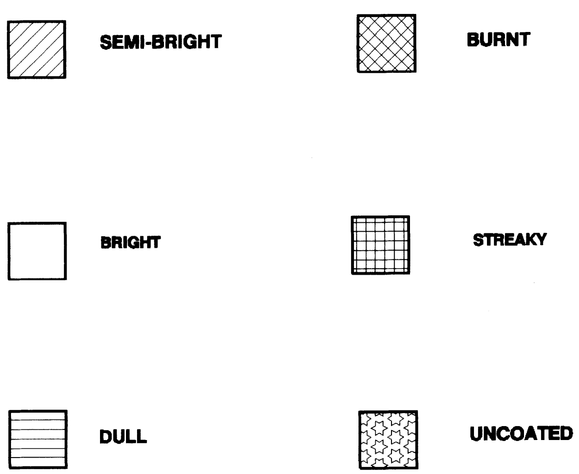

Fig. 1 Codes for recording Hull cell patterns

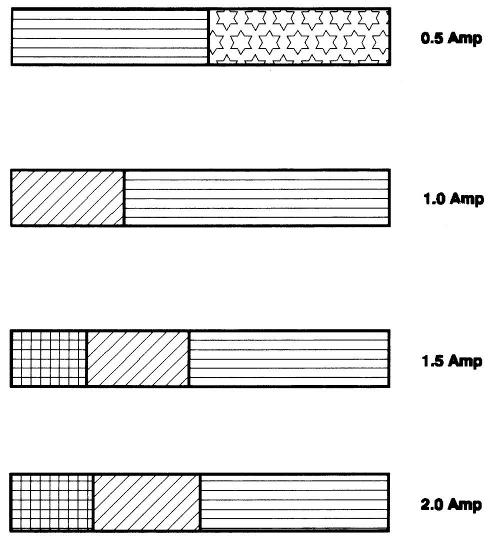

Fig. 2 Effect of cell current

The effect of temperature was studied by operating the bath at pH 10 at 1 A cell current. At 303 K a semi-bright pattern was found at 2–4 A dm^{-2}, whereas a further rise in temperature gave a rough and burnt deposit from 3.0 A dm^{-2} (Fig. 4).

From the above studies, the optimum conditions for obtaining a smooth fine-grained semi-bright deposit were found to be 2–4 A dm^{-2}, 303 K and pH 10.

Effect of additives

The caffeine concentration was varied from 0.5 g/l to 2.0 g/l and the pattern of the deposit is shown in Fig. 5. The presence of 0.5 g/l gave only a semi-bright deposit. With 1.0 g/l a bright pattern was found over a wide current density range between 2 and 4 A dm^{-2}. Further addition, however, narrowed the bright range, with a

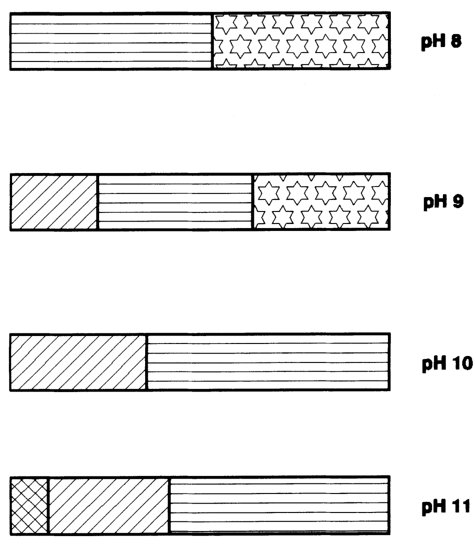

Fig. 3 Effect of pH

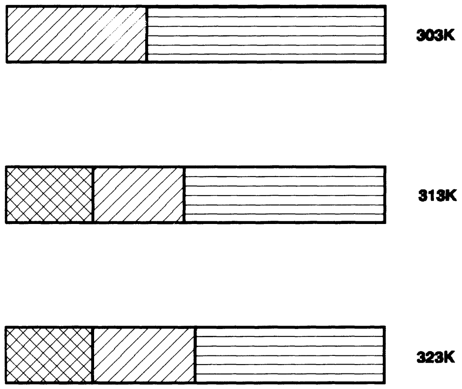

Fig. 4 Effect of temperature

burnt deposit above 4 A dm^{-2}. Thus 1.0 g/l caffeine was found as optimum to give a bright deposit at 2–4 A dm^{-2}.

The pattern of the deposits obtained with vanillin is shown in Fig. 6. Addition of 0.5 g/l gave a semi-bright deposit whereas 1.0 g/l addition resulted in bright deposits. With 1.5 g/l vanillin the bright range was observed between 1.5 and 4 A dm^{-2} . Further additions reduced the bright range and a burnt deposit was found above 4 A dm^{-2}.

Throwing power

The throwing power of a solution depends upon the shape of the cathode, the arrangement of the electrodes, the presence of organic additives and polarization at a metal discharge [9]. Deposition from a highly complexed solution such as cyanide-based electrolyte takes place at higher cathode potentials and hence associated with good throwing power, and vice versa with an acid-based

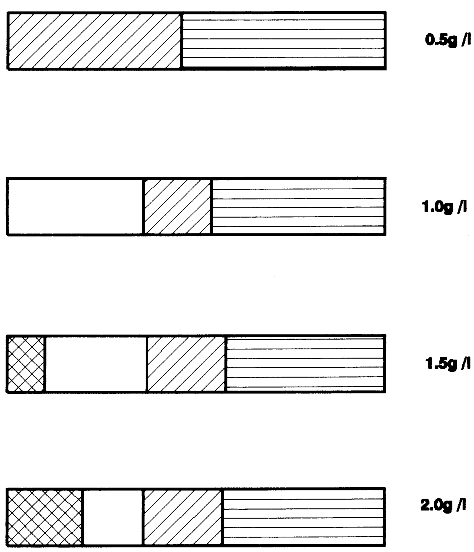

Fig. 5 Effect of caffeine

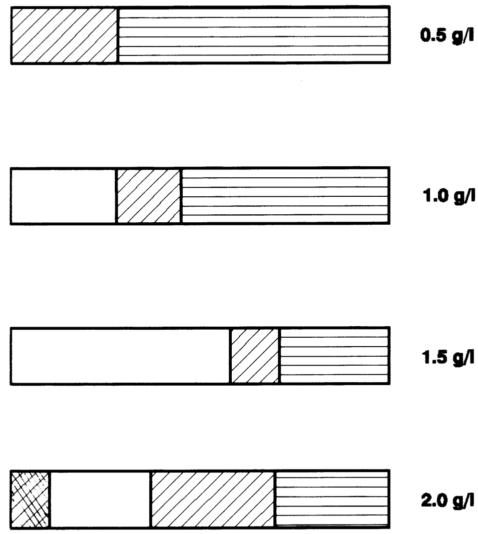

Fig. 6 Effect of vanillin

electrolyte. A throwing power of about 50% for cyanide zinc and 6% for acid zinc-based electrolyte has been reported [10]. In the present investigation, the throwing power was found to be about 23% under optimum conditions. This seems to be equal to that of a nitrilotriacetic acid-based zinc solution but higher than that of the acid zinc electrolyte [11]. Thus zincate solutions are found inferior to cyanide solutions but definitely superior to acid solutions with respect to throwing power. Caffeine and vanillin additions were found to improve slightly the throwing power, but an increase in current density, pH or temperature showed a considerable decrease in throwing power.

Current efficiency

The current efficiency of the zincate solution was measured at different current densities. At 303 K the current efficiency increased slightly with current density and at 3–4 A dm^{-2} it was about 63%. With further increases in current density, a decreasing trend was observed. Thus zincate solutions are found to be less efficient when compared with acid and cyanide electrolytes.

Conclusions

Optimum plating conditions and brightener concentrations to obtain a smooth and fine-grained bright zinc deposit for the non-cyanide alkaline zinc bath was found to be 2–4 A dm^{-2} at 303 K and pH 10. Brighteners are optional and their concentration would be of 1 g/l caffeine or 1.5 g/l vanillin. The electrolyte had about 63% current efficiency and 25% throwing power under optimum conditions.

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