ELECTRODEPOSITION OF ZINC-MANGANESE ALLOY FROM SULPHATE-CITRATE BATH

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Zinc-manganese alloy has better corrosion resistance than the individual metals. Hence, in place of pure zinc, zinc-manganese alloy coatings can be used to protect steel against corrosion. It is reported that zinc-manganese alloy containing 0-90% manganese could be electrodeposited from the sulfate-citrate bath. Most of the work reported are patented. Hence, in this paper the authors have made an attempt to deposit zinc-manganese alloy from a sulfate-citrate bath and studied in detail the bath development, alloy composition, cathode efficiency and cathode polarisation.

Key words : Zinc manganese alloy, sulphate-citrate bath, electrodeposition, alloy composition, cathode efficiency, cathode polarisation, addition agents, SEM study

INTRODUCTION

Zinc and its alloys have been used to protect steel against corrosion. Zinc-manganese alloy coatings from a sulphate bath containing organic salts of hydroxy acids and boric acid or sodium citrate, are highly corrosion resistant [1-4]. The zinc-manganese alloy containing 0-90% could be electrodeposited from a sulfate-citrate bath at a current density range of 1-5 A.dm^{-2} [5]. It is reported that such an alloy containing 40% manganese is possible with an efficiency of 60% from a sulfate-citrate bath under flow conditions [6]. The reported [5] corrosion studies show that log of time for appearance of rust is related linearly to manganese content of the coating upto 60% manganese, and the maximum time for the appearance of rust is 100 and 300 hours for coating thickness of 20 and 10 g.m^{-3} respectively. In this paper, authors have attempted to deposit zinc-manganese alloy from sulfate-citrate bath and studied in detail bath development, alloy composition, cathode current efficiency and polarisation.

EXPERIMENTAL

Stainless steel or graphite suitably bagged in a filter paper and cloth was used as the anode for Hull cell experiments. The pretreatments for mild steel included degreasing and etching in 10% hydrochloric acid at 313 K for 60-120 secs. The electrolyte was prepared as follows: manganese sulfate, zinc sulfate and trisodium citrate were dissolved in distilled water separately. Known quantities of zinc sulfate and trisodium citrate were mixed, digested for 8 hrs, cooled, mixed with known amount of manganese sulfate, filtered, made up to the required volume and the required amount of gelatin was added as an addition agent.

Bath composition was arrived at from Hull cell studies. The alloy deposition was carried out on mild steel cathode in a H-type glass cell with glass frit as a separator. Deposits, plated on stainless steel, were analysed by colorimetric and EDTA titration methods [7]. Alloy efficiency was calculated from the weight of the deposit and coloumbs passed. Effects of current density (c.d.), pH, temperature, manganese and zinc contents of the electrolyte and manganese content of the deposit were studied. Cathode polarisation studies were made, and using the efficiency and alloy composition, partial polarisation curves were drawn. The adhesion of the coating was tested by bend test.

RESULTS

Hull cell studies

Effect of pH and temperature

Effect of pH on Hull cell pattern (data not included) in the bath containing: Mn 20, Zn 10, citrate 200 g dm^{-3} shows that at pH 4.5, the deposit is grey in the c.d. range 0.6 - 4.0 A.dm^{-2} and dull thereafter. At pH 5.5, grey deposit occurs in the low c.d. region upto 1 A.dm^{-2}. A further rise of pH to 6.5, leaves the grey deposit zone unaffected but reduces slightly the dull deposit range.

Increase in electrolyte temperature in the range 309 to 323 K narrows down the c.d. range of the dull deposit, keeping the grey deposit pattern nearly same.

From these studies, a pH of 5.5 and bath temperature of 309 K were chosen from the view point of widest c.d. range for dull deposit.

Effect of metal ion concentration

Variation of zinc and manganese contents of the bath of pH 5.5 at 309 K in the ranges 5-20 and 20-30 g.dm^{-3} respectively, indicates that 5-10 g.dm^{-3} of zinc produces dull deposit in the range of c.d. of 1-8 A.dm^{-2} while increase of manganese content from 10-30 g.dm^{-3} steadily decreases the high c.d. limit of grey deposit, with the widest range of 1-8 A.dm^{-2} for dull deposit at 20 g.dm^{-3} of manganese . (Data not presented). To sum up, zinc and manganese contents of 10 and 20 g.dm^{-3} respectively are optimum leading to widest dull deposit zone.

Effect of citrate concentration

It can be seen from Fig.1 that increase in citrate concentration from 100 -300 g.dm^{-3}, decreases the c.d. zone of grey deposit and shifts the dull deposit pattern towards low c.d. areas. Widest dull deposit pattern was obtained at 200 g.dm^{-3} of citrate in the bath.

Effect of addition agents

It can also be seen from Fig.1 that addition of gelatin or agar-agar improves the appearance of both dull and grey deposits to semi-bright and dull deposits respectively. Addition of 0.1 g.dm^{-3}

selenic acid produces deposits of different looks over the Hull cell c.d. range.

Alloy efficiency and composition

Effect of pH

Increasing electrolyte pH increases the cathode current efficiency (CE) as well as manganese content of the alloy deposit (Fig.2).

For a pH change from 4.5 to 6.5, the efficiency increase is from 44 to 80% and increase in manganese content in the deposit is from 2 to 3% at 1 A.dm^{-2}, but at 8 A.dm^{-2} they are 8 - 16 and 46-71% respectively.

Fig. 1 : Effect of citrate conc. g.dm^{-3} (a) 100 (b) 200 (c) 300 effect of addition agent mg.dm^{-3} (d) gelatin 200 mg/l (e) agar- agar 20 (f) selenic acid 100 mg/l bath g.dm^{-3} Mn 20; Zn 10; temp 309K pH 5.5
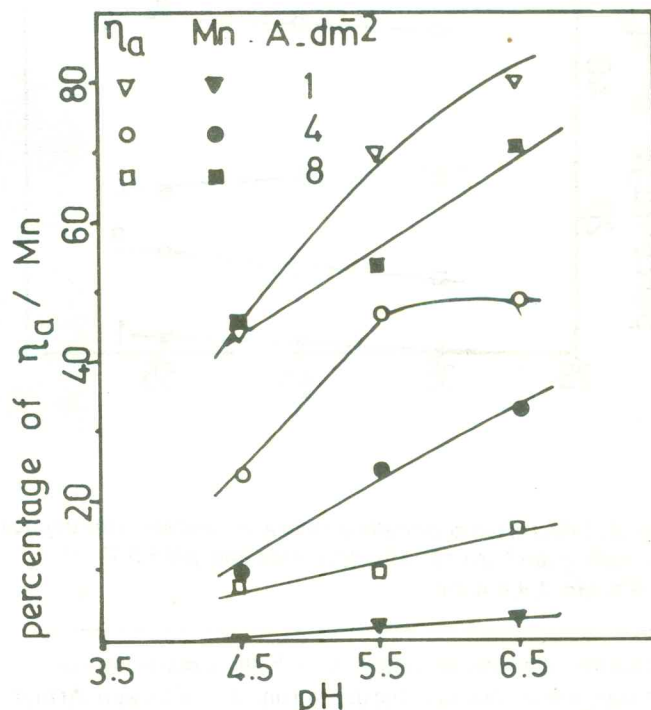

Fig.2 : Effect of pH on cathode efficiency and Mn in the deposit bath g.dm^{-3} Zn 10; Mn 20; citrate 200; 309K

Effect of temperature

The effect of solution temperature on CE and manganese content of the alloy (Fig.3) shows that not much change in efficiency and alloy composition are observed with rise in bath temperature.

Effect of manganese concentration in bath

Figure 4 shows the effect of manganese concentration in bath on the CE and manganese content of the deposit. It can be seen that
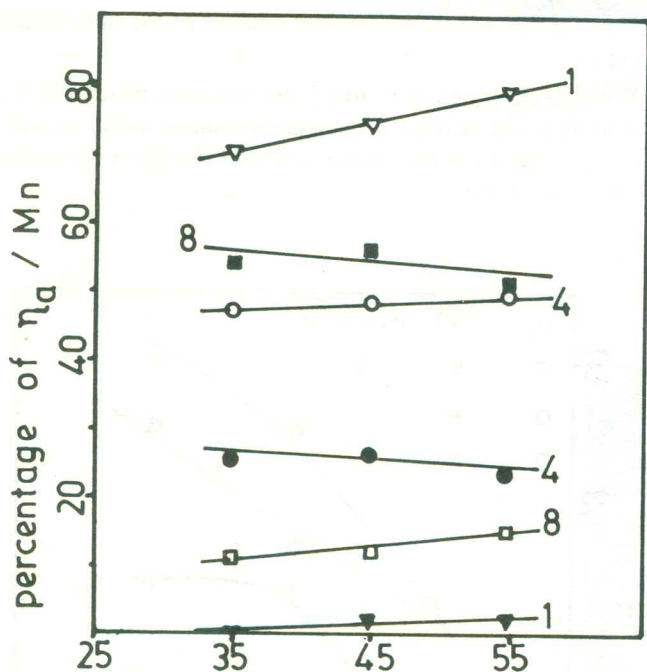

Fig. 3 : Effect of temp. on cathode efficiency and Mn in the deposit % bath g.dm^{-3} Zn 10; Mn 20; citrate 200; pH 5.5 ∇ $\circ$ $\Box$ η_a; ∇ $\bullet$ $\blacksquare$ Mn; 1,4,8 A.dm^{-2}

Fig. 4 : Effect of Mn in bath on η_a and Mn in the deposit % bath g.dm^{-3} Zn 10; citrate 200; pH 5.5; temp. 309K

increasing manganese content in the bath increases, in general, the manganese content of the deposit and the CE as well. At high c.d. of 8 A.dm^{-2} however, the efficiency is almost constant at all manganese concentrations in the bath.

Effect of zinc concentration in bath

Zinc content of the electrolyte greatly affects the alloy composition and CE (Fig.5). Increase in zinc content increases the efficiency with simultaneous decrease in manganese content of the deposit. For an optimum concentration of 10 g.dm^{-3} of zinc, the CE is 47% and manganese content of the deposit is 25% at 4 A.dm^{-2}.

Effect of citrate concentration in bath

Citrate content of the electrolyte greatly influences the CE and manganese content of the deposit (Fig.6). At a c.d. of 4 A.dm^{-2}, increase in citrate concentration from 100 to 300 g.dm^{-3} incre-
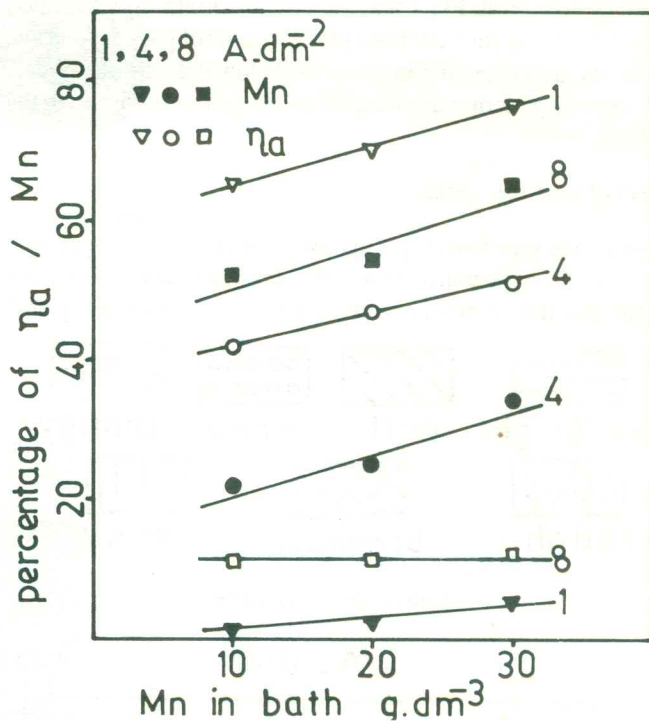
ases the manganese in the deposit from 17 to 30% and decreases CE from 50 to 40% and the change in efficiency is lower at 8 A.dm^{-2}. In general, increase in citrate concentration increases the manganese content of deposit and decreases the efficiency.

Effect of current density

It can be seen from the Fig.7 that increasing c.d. from 1-10 A.dm^{-2} increases the manganese content of the deposit from 2 to 72% and decreases the CE from 72 to 6%.

Galvanostatic polarisation

Figure 8 shows the total polarisation behaviour for zinc, manganese and zinc-manganese alloy deposition along with hydrogen evolution. Polarisation for zinc deposition is much more than that of manganese and zinc-manganese alloy deposition. It can be seen that there is a cross over point at -1.7 V (SCE) and 3 A.dm^{-2}. At this point, the corresponding efficiency is about 55% with a manganese content of 25%. The partial polarisation curves (Fig.9) clearly indicate the resultant alloy composition at various c.ds.and/or potential. For an optimum bath composition, the limiting c.d. values for zinc and manga-
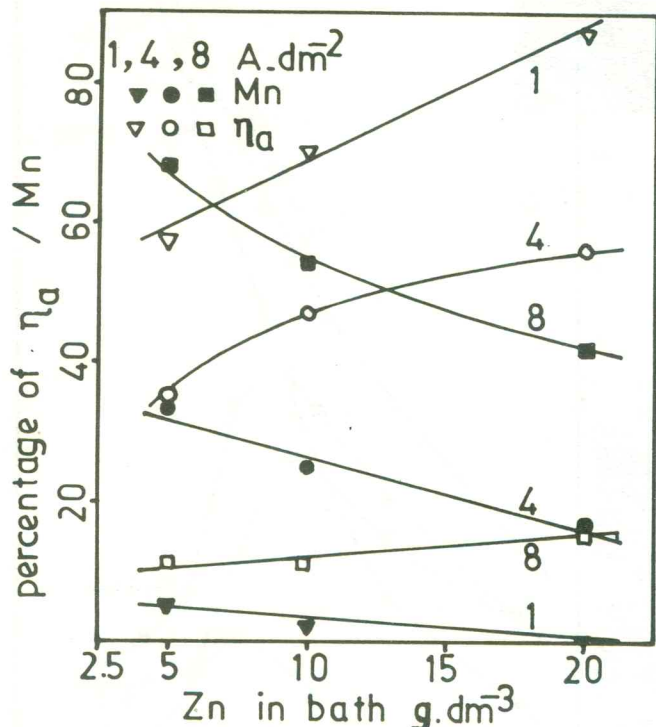
Fig. 5 : *Effect of Zn in bath on η_a and Mn in the deposit % bath g.dm^{-3} Mn 20; citrate 200; pH 5.5 temp 309K*
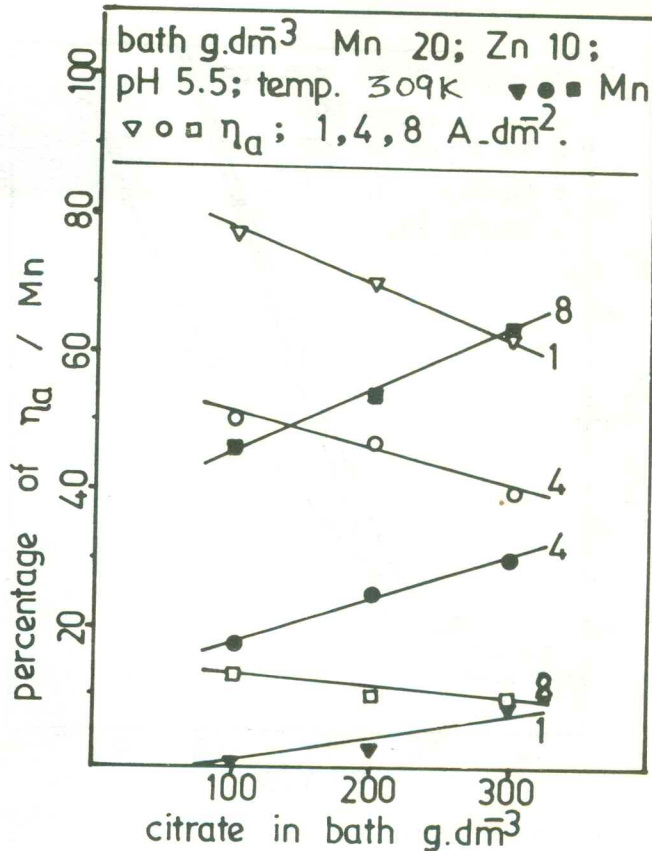

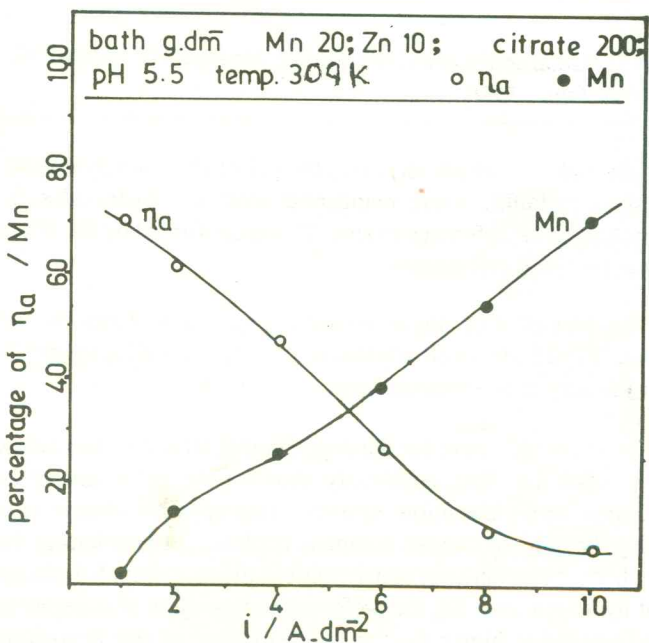Fig. 6 : *Effect of citrate conc. in bath on η_a and Mn in the deposit % citrate in bath g.dm^{-3}*

Fig. 7 : *Effect of current density on cathode current efficiency and Mn in the deposit %.*

nese deposition from the alloy baths are 1.4 and 0.6 A.dm^{-2} with corresponding potential of -1.7V and -1.8V respectively. The cross over of partial polarisation curves for zinc and manganese deposition is at about 0.5 A.dm^{-2} and 1.87 V. A 50:50 alloy is produced only at this potential with corresponding total c.d. of 7.8 A.dm^{-2} and not at the cross over point in total polarisation curve (Fig.8). It can also be seen from Fig.9 that beyond the limiting c.d., the zinc content of the deposit is reduced steeply with c.d., whereas the manganese content decreases steadily. Hydrogen curve crosses the curve of zinc near to its peak c.d. Qualitatively, this can indicate a higher % of zinc in the deposit. Only pure zinc is being deposited at very low c.ds. In other words, for zinc-manganese alloy deposition to take place even when manganese ion concentration is 67% of the total metal concentration, high c.ds. have to be applied.

SEM studies

Deposits of 15 to 20 μm thick were produced from the bath developed at various c.ds.and the SEM topographies (Figs.10 to 12) show that big grains are seen in the manganese deposits and flake-like structure is seen in zinc deposit. Zinc-manganese alloys containing less than 25% manganese show fine grained
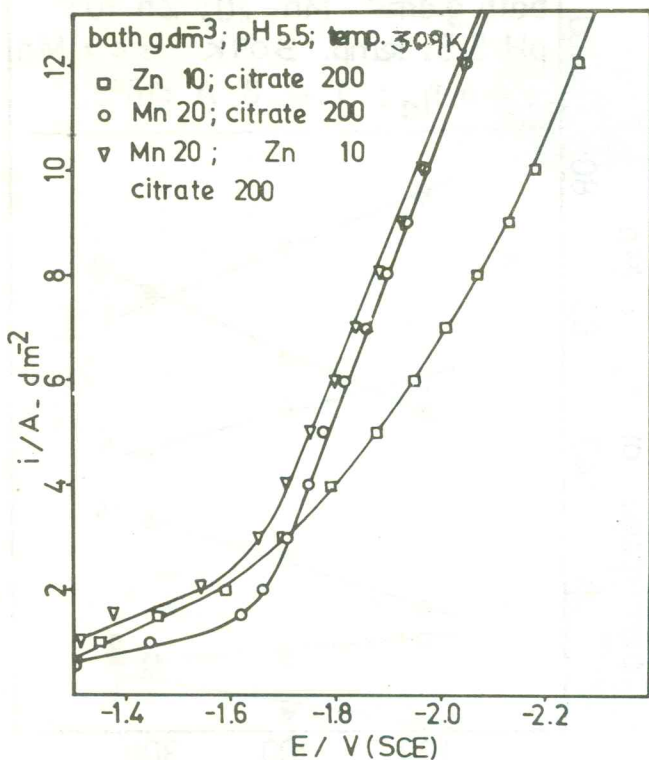
Fig. 8 : Total polarisation

Fig. 9 : Partial polarisation bath g.dm-3 ; Mn 20 ; Zn 10 ; citrate 200 ; pH 5.5; temp. 309K

structure and alloys of more than 25% manganese show somewhat bigger grains with layer-like structure.

DISCUSSION

In the present study on zinc-manganese alloy deposition from a sulfate-citrate solution, zinc is nobler than manganese. Hence, zinc forms stabler complexes with citrate than manganese. Further, increasing the concentration of the complexant or decreasing the zinc ion concentration in bath, shifts the deposition potential of zinc in the less noble direction and favours the deposition of manganese. However, increasing manganese content in the electrolyte no way influences the deposition towards increased manganese. In this alloy deposition, manganese starts depositing at potentials > -1.3V (SEC). Bath temperature brings slightly more zinc ions to the cathode favouring marginally higher zinc deposition and cathode CE.

The partial polarisation curve of hydrogen crossing that of zinc at its peak potential qualitatively indicates the higher percentage of zinc in the deposit upto the limiting c.d. of zinc. Beyond the cross over point of the partial curves of zinc and manganese, at high c.ds. (> 10 A.dm^{-2}), the deposit is streaky/gre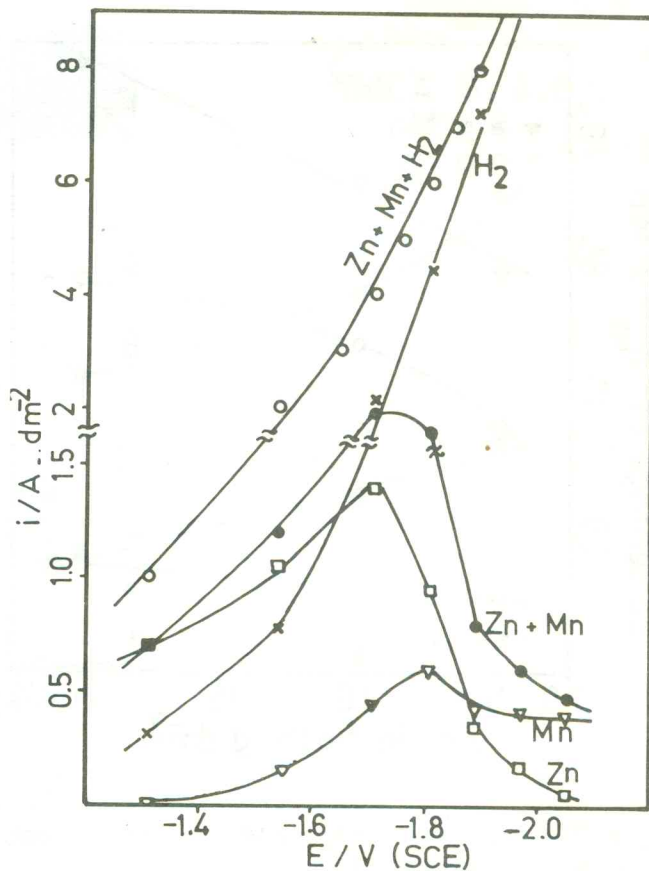yish in nature. This may be due to the evolution of hydrogen at the cathode, which increases the pH of the catholyte (with respect to bulk), where manganese from its hydroxides is discharged in preference to zinc. This is confirmed by the effect of pH on Hull cell pattern.

The plot of % of zinc in the deposit against % of zinc in the bath (Fig.13) shows clearly that zinc-manganese alloy system is of the normal codeposition type.

However, the curve for the deposition at 10 A.dm^{-2} lies below the reference line, apparently showing the behaviour of an anomalous codeposition system. This apparent change over may be due to almost complete depletion of zinc ions at the cathode diffusion layer and increase in pH due to rapid discharge of hydrogen ions. So, the preferential deposition of manganese is favoured at high c.ds. not at the expense of zinc deposition but due to the paucity of zinc ions at the interface.
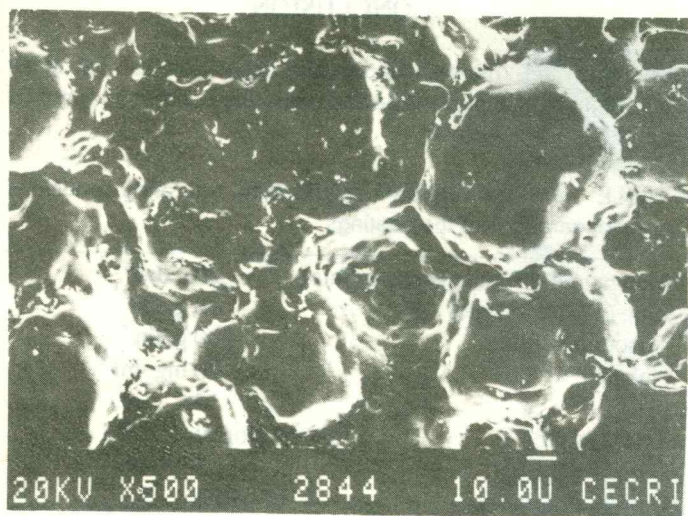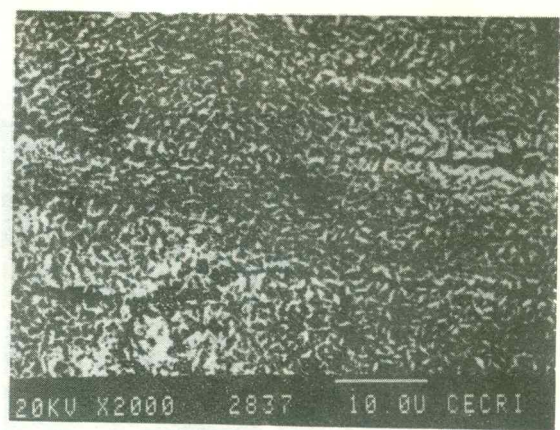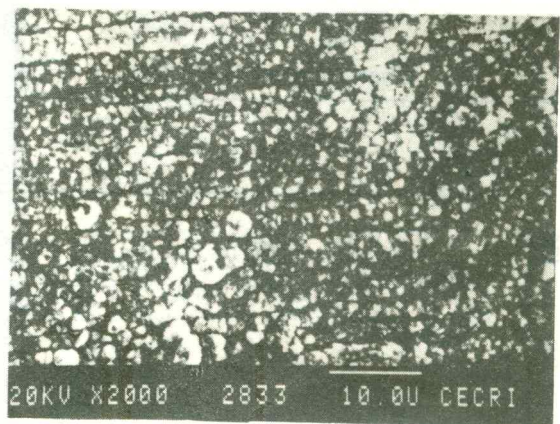
Fig. 10 : SEM Photomicrograph
Manganese

Zinc

Fig. 11 : SEM Photomicrograph
Zinc-Manganese (2.4%)

Zinc - Manganese (14.3%)

Zinc - Manganese (24.8%)

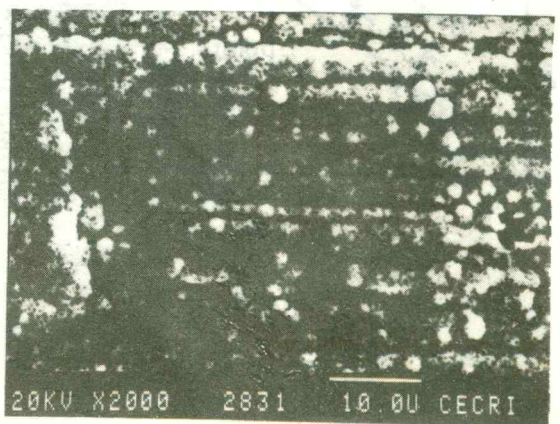Fig. 12 : SEM Photomicrograph
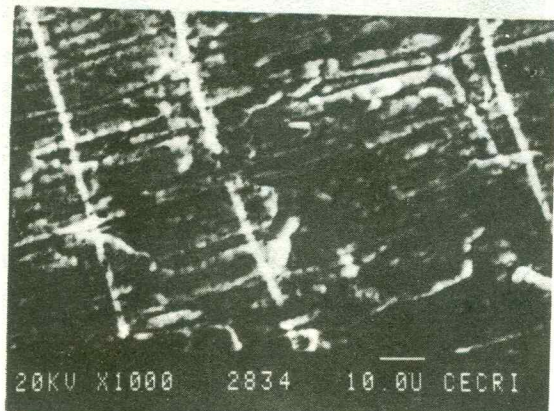Zinc - Manganese (37.5%)

Zinc - Manganese (54.1%)

Fig. 13

CONCLUSION

The study on zinc-manganese alloy deposition has led to an optimum bath composition and operating conditions summed up in Table IV below:

TABLE - IV: Optimum bath composition, operating conditions and appearances of the coatings

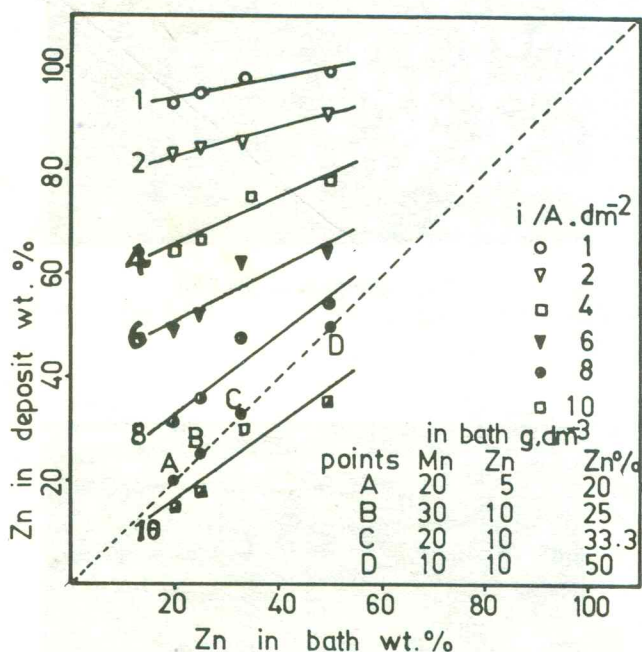|	
Manganese (as manganese sulfate)	20 g.dm^{-3}
Zinc (as zinc sulfate)	10 g.dm^{-3}
Trisodium citrate	200 g.dm^{-3}
Gelatin	20 mg.dm^{-3}
pH	5.5
Temperature	Ambient (309K)
Current density	1 - 8 A.dm^{-2}
Current efficiency	10 - 70%
Alloy composition	2 - 55% manganese

Appearance of the coating over a current density range is

(i) dull deposit at 0.1 - 1.7 A.dm^{-2}, corresponding manganese in the deposit is 0 - 10%.

(ii) semibright deposit at 1.7 - 8 A.dm^{-2}, corresponding manganese in the deposit is 10 - 55%.

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