Studies on the Electrodeposition of Cobalt-Manganese Alloys from Fluoborate Bath

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Cobalt-manganese alloys have been electrodeposited from fluoborate bath. The effect of bath composition, pH and temperature on the alloy composition has been studied Glycine and ammonium selenate were added to get good quality alloy deposits in broader current density range. Only cobalt-base alloys are obtained from 20 wt.% Mn bath For 80 wt.% Mn bath containing glycine and ammonium selenate, two ranges of current densities were observed, where either cobalt-base or manganese base alloys are electroplated. Thicknesses upto 25 μm are easily deposited from 20 wt.% Mn bath cantaining glycine and citric acid, but 80 wt.% Mn bath gives only 6-8 μm thick alloy deposits. Current efficiency of alloy deposition is low. X-ray studies revealed line broadening especially for Mn-base alloys. Polarization studies revealed that at a given cathodic potential deposition of the alloy is more favourable than the deposition of pure Mn alone

Electroplated cobalt alloys are gaining importance because of their high temperature properties, corrosion resistance and magnetic properties. The electroplated manganese alloys are useful as protective and decorative coatings for steel and other metals. Cobalt-manganese alloys have potential applications as wear resistant and oxidation resistant coatings. Electrodeposition of manganese alloys is also of interest because of its low cathode current efficiency of alloy deposition.

Brenner[1] has discussed in detail the deposition of manganese alloys with iron group metals from various baths. Ridell[2] et al investigated the electrodeposition of cobalt-manganese alloys from sulphate-citrate bath It was reported that satisfactory cobalt-manganese alloys could not be deposited from pyrophosphate and fluoborate solutions. There are references of cobalt-manganese alloy deposition from sulphate[3,4] and chloride baths[5].

In the present study, a detailed investigation was carried out on electroplating of cobalt manganese alloys from fluoborate bath. Effects of bath variables on the physical appearance, cathode current efficiency (C. E.) and composition of the cathode deposits were studied.

EXPERIMENTAL PROCEDURE

The fluoborate solutions for plating were prepared by dissolving manganese and cobalt carbonates in fluoboric acid. Platinum and copper strips were used as anode and cathode respectively. The electrolysis was carried out in a diaphragm cell to assist pH control of catholyte and to isolate anodic oxidation products that otherwise promote manganese alloy dissolution. The plating was carried out under static conditions. Preparation of the cathode strips and other experimental procedure have been reported earlier[6]. 75 ml. of fresh solution was taken for each experiment. The catholyte and the anolyte contained cobalt and manganese fluoborates, ammonium fluoborate and hydroxylamine hydrochloride Ammonium fluoborate was added to improve the quality of the deposit and for good conductance. To the anolyte, 20 gm/l sodium citrate was added to prevent the formation of a black coating of MnO_2 on the anode. Necessary additions like ammonium selenate, glycine and citric acid were made to the catholyte. Ammonium selenate is known to improve current efficiency (C. E.) in manganese plating bath. Sodium lauryl sulphate (0.1 g/l) was added to the bath as an antipit agent whereever glycine/citric acid was added as complexing agent. The maximum manganese concentration is restricted to 16 gm/l to avoid precipitation of double compound of manganese and ammonium fluoborate. Total metal concentration was fixed at 20 gm/l in the entire study. The time of electrolysis was varied from 6 to 30 minutes depending upon the current density,

The deposits were stripped using a mixture of dilute sulphuric acid and hydrogen peroxide. Copper was removed by H_2S precipitation. Total metal content was determined by first complexing it with EDTA and titrat-

ing the excess EDTA against standard zinc oxide solution using Eriochrome Black T as indicator, and the manganese was determined by EDTA titration after complexing cobalt with potassium cyamide solution[7]. The cathode potentials were measured against saturated calomel electrode. The sign of the potential is negative unless otherwise stated. The throwing number of the plating solution was calculated from the Gardam's Equation[8], $N = \frac{b}{2p}$ where b is the slope of the cathode potential—log current density curve and p is the resistivity of the plating solution.

RESULTS AND DISCUSSION

Electrodeposition was carried out under different conditions with respect to bath composition, current density, pH, temperature and other bath additions, and the results of these variables on deposit composition, current efficiency and the quality of the deposits, have been presented in Table I to III and Figures 1 to 7.

Detailed studies were first carried out using 20 wt.% Mn bath. Results of these studies have been tabulated in Table—I.

TABLE—I Effect of various Additions on % Mn and C.E.

Bath : 20 wt % Mn, Co + Mn 20 gpl, Ammonium Fluoborate 110 gpl, Hydroxylamine hydrochloride 2 gpl, pH = 3, Temperature = 25°C. C.D. A/dm² 4-30

Bath No.	Additions to the catholyte	Range of % Mn in deposit	C.E %	Remarks
I	Ammonium Selenate 0.5 g/l	4.3–5.1	63.5–25.3	4 to 8 A/dm²-deposits flaking. 12-16 A/dm²-smooth, adherent, grey coating. 20 A/dm²-Flaking, burning of alloy deposit at edges. > 20 A/dm²-only black coating.
II	Bath-I + Glycine 35 gpl, Sodium lauryl sulphate 0.1 gpl	4.4–6.5	53.5–11.9	4-12 A/dm²-smooth, adherent dull grey coating. Slight burning at edges at 8-12 A/dm². 16 A/dm²-Alloy coating grey in centre, black at edges. 20 A dm²-Black coating polished to reveal grey coating. > 20 Adm²-Only black coating.
III	Bath-II + citric acid 30 gpl	3.8–7.6	43.2–18.8	4–8 Adm/²-Smooth, steel grey adherent alloy coating. 12 A/dm²-Same as above but slight flaking at one end. 16 A/dm²-Smooth, adherent, slight burning at edges. 20 A/dm²-smooth, adherent, considerable burning at edges. > 20 A/dm²-only black-coating.

The bath containing glycine, citric acid and ammonium selenate (Bath III) gave better quality deposits, hence the effect of bath pH and temperature was studied using this bath. pH 2 and 4 are detrimental in the

operation of the bath, since considerable flaking was observed. Black film covered the deposits obtained at pH 2. Flaking tendency was negligible if bath III was operated at pH 3 and temperature 40°C. Smooth and adherent alloy deposits were obtained at pH = 3 and temperature 50°C. The common feature of all the parameters studied is that the maximum manganese in the deposit is only 7.6 wt. per cent, even though the bath contains 20 per cent.

Different baths containing 40, 50 and 60 wt. % Mn along with additives as given in Bath II, were made up. The baths were operated at pH = 3, 25°C. Satisfactory alloy deposit was obtained only at 4 A/dm² from 40 wt.% Mn bath, beyond which black film started appearing on the alloy deposits. It was not possible to operate the bath beyond 20 A dm². The deposits obtained from 50 and 60 wt. % bath were all covered with black film in the entire C. D region of 4-40 A/dm². The black coating was polished to reveal dull grey alloy coating underneath. The maximum percentage manganese in deposit was 12.2% which was obtained from 60 wt.% Mn bath at 40 A/dm².

A few baths were made containing 80 wt. % Mn in solutions, and the results are presented in Table II and Figures 1 and 2

TABLE—II Effect of Bath Additions on Quality of Deposits

Bath : 80 wt.% Mn, Co + Mn 20 g/l, Amm. fluoborate 110 gpl, $NH_2OH.HCl$ 2 gpl, pH - 3, Temperature 25°C.
C.D. A/dm² 2-40

Bath No.	Additions to the catholyte	Remarks
IV	Ammonium Selenate 0.5 gpl	> 6A/dm², grey, metallic flaking alloy coating. 6-12 A/dm² : Black coating polished to reveal dull grey coating. > 12 A/dm² : only black deposits.
V	Glycine 35 gpl, sodium lauryl sulphate 0.1 gpl	Unsatisfactory alloy deposited upto 20 A/dm², either flaking or covered with black oxide film, below which flash grey alloy coating visible. > 20 A/dm² : Only black coating
VI	Bath-V + Amm Selenate 0.5 gpl	2 A/dm² : Grey metallic layer 4-12 A/dm² : Grey coating covered with black film 16-40 A/dm² : Smooth, shining grey, adherent alloy coating
VII	Bath-VI + citric acid 30 gpl.	Smooth, steel grey, adherent alloy coating at all current, densities.

Strong dependance of the nature of deposit was found on both bath additions and current densities. The manganese content in the deposit increases gradually at low current density regions, with an abrupt increase at 26 A/dm² for bath VI. Same sudden increase in manganese content of the deposit was noticed at 30 A/dm² for bath VII (Fig. 1). Intermediate alloy compositions (25 — 54 wt.% Mn) could not be deposited even though C. D was gradually varied from 2 A/dm² to 40 A/dm². There are two ranges of current densities : the region of Co-base alloy and the region of Mn-base alloy. Addition of 30 gms/l citric acid to the bath, gave smooth better quality deposits, but it lowered the C E. of alloy deposition which is illustrated in Fig 2. Glycine-citric acid bath gave smooth deposits in the entire C.D. region but gave Co-base and Mn-base alloys, no intermediate alloy composition could be deposited at 2-40 A/dm².

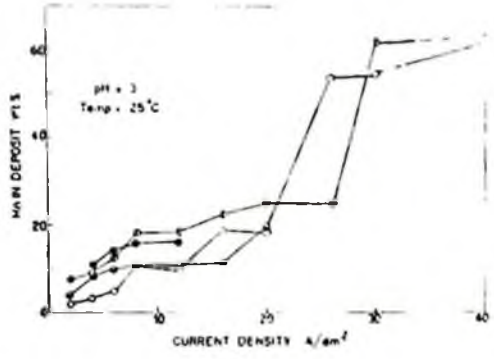


Fig. 1 : Effect of Bath additions on percentage Mn in the deposit : 80 wt.% Mn Bath, ● Bath—IV, Bath-V, ○Bath.VI, θ Bath-VII.

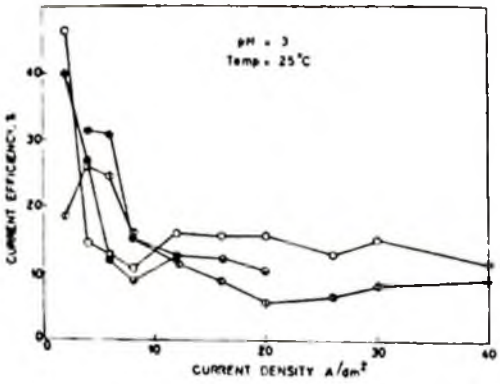


Fig. 2 : Effect of Bath additions on Current Efficiency : ● Bath-IV, Bath-V, ○Bath-VI, θBath-VII.

Since satisfactory alloy deposits were obtained from bath VI, further studies were carried out with this bath to find the effect of ammonium fluoborate and ammonium selenate concentrations and also the effect of bath pH and temperature on the quality, composition and C E. of alloy deposition, and the results are given in Figs. 3—5

It was not possible to operate the bath beyond 12 A/dm² without ammonium fluoborate additions, in this C.D. range, black deposits were obtained which were polished to reveal dull grey alloy coating. Baths containing 50-150 gms/l ammonium fluoborate gave smooth, adherent and grey deposits in the 26–40 A/dm² C.D. range. Bath with 110 g/l NH_4BF_4 addition gave best results as good deposits were obtained in the 16-40 A/dm² current density range. The manganese content of the deposit decreases with ammonium fluoborate concentration in the bath (fig. 3). The decrease in the manganese content of the deposit was pronounced in the higher current density region. In fact non Mn-base alloy could be deposited from the bath containing 150 gms/l of ammonium fluoborate in the C.D. region of 26-40 A/dm². The maximum manganese content of the deposit was 31.5% at 40 A/dm² for the bath containing 150 gms/l of ammonium fluoborate in sharp contrast to the manganese content of 84.5% for the bath containing 50 gms/l of ammonium fluoborate. This is possibly due to stabler compound formation between the manganese and the ammonium compound lowering the manganese content of the deposit. Sveshate[3] et. al. observed that the composition of the alloy remained independent of the variation in the concentration of ammonium sulphate between 50—200 gpl. It was observed that the addition of ammonium fluoborate was essential to promote the deposition of manganese by keeping the cathode surface active (depassivating). It also helped to increase the bath conductivity. The typical values for bath voltages were 13.7 V and 6.3 volts for bath containing nil and 150 gms/l ammonium fluoborate respectively. The effect of concentration of ammonium fluoborate (50/150 gms/l) on the C.E. of alloy deposition was negligible.

Ammonium selenate has beneficial effects on the quality of electrodeposits. No deposit was obtained beyond 20 A/dm² without ammonium selenate addition (Table II, Bath V). The effect of ammonium selenate concentration on C.E. was pronounced in the high C.D.

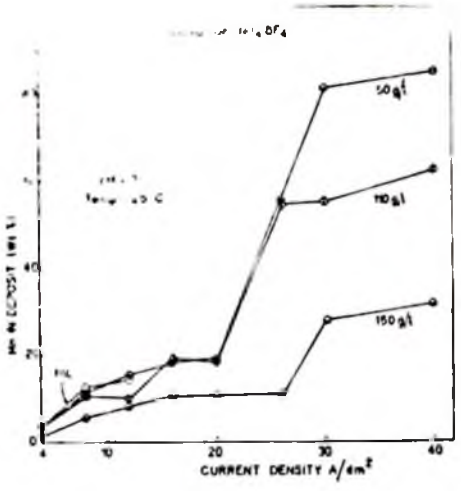


Fig. 3 : Effect of Ammonium fluoborate concentration on Deposit Composition for Bath-VI.

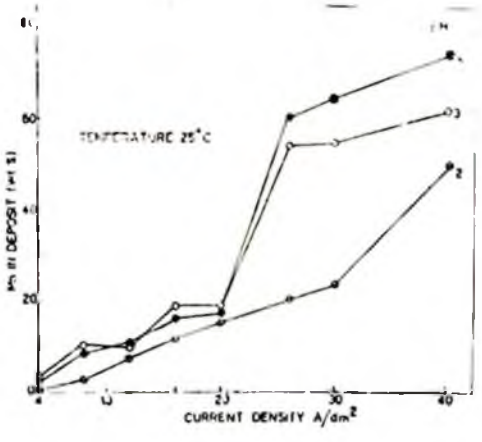


Fig. 4 : Effect of Bath pH on Deposit Composition for Bath-VI.

region. The C E of alloy deposition falls from 15.4% to 4.1% at 30 A/dm² and from 11.2% to 2.4% at 40 A/dm² for baths containing 1.0 gm/l and 0.1 g/l ammonium selenate respectively.

Manganese content of the deposit increases with pH 2 to 4 in the C.D. range of 26-40 A/dm² (Fig. 4). But pH 3 was found to be best with respect to the physical appearance of the electrodeposits.

The percentage of manganese decreases with temperature (Fig. 5) and the quality of the deposits deteriorated rapidly as the bath temperature was increased from 25°C to 50°C. The coatings obtained at 50°C in the entire C.D. range of 4—40 A/dm² were covered with black film, which on polishing revealed grey metallic coating. The C.E. of alloy deposition decreased with the increase in bath temperature.

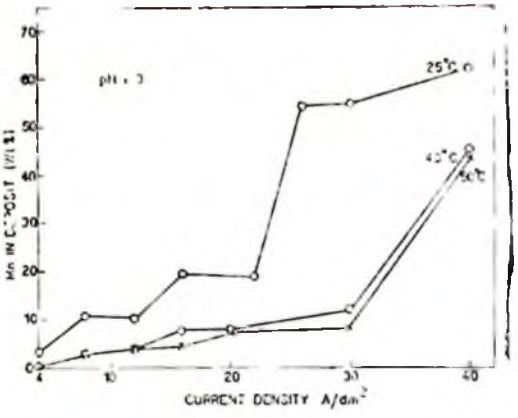


Fig. 5 : Effect of Bath Temperature on Deposit Composition for Bath VI.

After carrying out the detailed studies of the effect of bath composition, pH, temperature and the variation in the concentration of ammonium fluoborate and ammonium selenate from 80 wt.% Mn bath containing glycine and ammonium selenate (Bath VI), it was observed that the behaviour of two ranges of current densities, the region of Co-base and the region of Mn-base alloy, is common for all the para-metres studied. In general the variation in C. D. from 4 – 20 A/dm² gave Co-base alloys and 26 to 40 A/dm² gave Mn-base alloys. No intermediate alloy composition (25 – 45 wt.% Mn) could be electroplated with the exception of the bath containing 150 gms/l ammonium fluoborate where the deposited alloy had maximum manganese content of 31.5% at 40 A/dm². In the Intermediate current density region 4-16 A/dm², the alloy plating process appeared to be unstable as the deposits were found to be covered with black oxide film which on polishing revealed dull grey coating of the alloy. While studying the effect of bath temperature, it was found that the region of current density, where coating covered with black film is obtained, became wider with the increase bath temperature. It was possible to operate the bath beyond 40 A/dm², smooth, silver grey deposits were obtained at 50 A/dm² from Bath VI.

In general, C.E. of alloy deposition is more for alloys deposited from 20 wt.% Mn bath compared to 80 wt.% Mn bath under comparable conditions of electrodeposition.

Thick Deposits :

A number of electroplating experiments were carried out from baths VI and VII, taking 300 ml each of catholyte and anolyte, and carefully controlling the bath pH at 3 and temperature 25°C with varying time at current densities ranging from 16 to 40 A/dm², but it was not possible to obtain electroplates thicker than 6—8 μm. Electrodeposits were found to be covered with black film if electrolysis was continued for longer time to get deposits thicker than 6-8 microns. This is believed to be due to intense evolution of H_2 during alloy deposition (C.E. of alloy deposition is low) leading to alkalization of the solution in the vicinity of cathode, which contributes to the formation of gels of the co-deposited metal hydroxides on cathode surface that they cannot be reduced and the cathode surface is passivated and consequently only poor quality deposits are obtained[10, 11].

It was possible to electrodeposit 10–15 μm thick alloy deposit from Bath II by operating at pH = 3 and temperature 25°C at current density ranging from 4 A/dm² to 20 A/dm². Twenty to twentyfive microns thick alloy coatings could be deposited from bath III at pH = 3 and temperature 50°C and C.D. 4-20 A/dm². The deposits started cracking and burning at the edges of the electrodeposits were noticed if electrolysis was continued to get deposits thicker than 1 mil.

Cathode Potential :

Figure 6 presents the cathode potential curves of

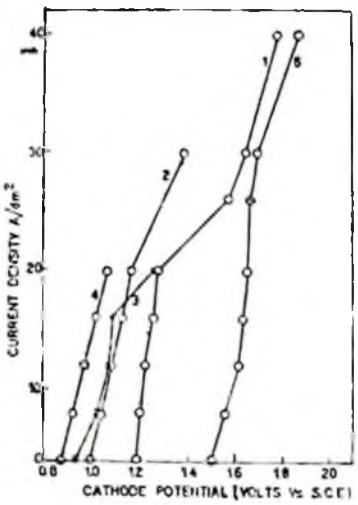


Fig. 6 : Cathode Potential curves for Co-Mn alloys and for pure Manganese : Curve 1 : Bath-VI, pH 3, 25°C Curve 2 : Bath-VI. pH 3, 50°C ; Curve 3 : Bath-II, pH 3, 25°C : Curve 4 : Bath-III, pH 3, 25°C ; Curve 5 : Pure Mn 16 g/l, other additions same as in Bath-VI, pH 3, 25°C.

Co-Mn system for baths II, III and VI under different experimental conditions. Polarization curve of pure manganese has also been included in the figure 6. The cathode potential during alloy deposition increased with increase in C D. and decrease in temperature There is abrupt shift in cathode potential towards active value (bath VI) signifying sharp rise in manganese content of the alloy. There is considerable polarization (0.5-0.9 V) during alloy deposition. From the alloy curve, composition and C.E. of alloy deposition, single metal potentials have been reconstructed. Fig. 7 presents the cathode potential curves of cobalt-manganese, pure manganese and the reconstructed potential curves of cobalt and manganese It is seen from the potential curves that the codeposition of manganese and cobalt is accompanied by greater depolarization than the deposition of Mn alone[9]. The calculated curve of cobalt is closer to alloy at lower current densities, indicating that a high-cobalt alloy is to be expected in this region. At higher current densities, the manganese curve comes closer to the alloy curve indicating the Mn-base alloys will be obtained in this region.

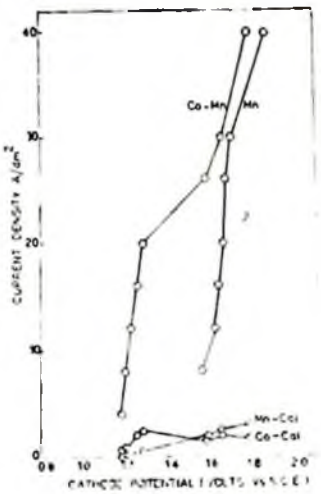


Fig. 7 : Reconstruction of single Metal Potential Curves from Alloy Composition, Alloy C.E. and Potential ; Bath Composition :

Pure Mn 16 gpl } pH 3, 25°C.
Alloy Bath-VI }

The bath possessed fairly good throwing power as observed visually and indicated by the throwing number (0.0121, calculated for bath II).

Structure and Hardness of the Deposits :

X-ray studies using CuKσ radiation at 36 KV and 18 mA showed line broadening for Co–Mn alloys containing varying percentage of manganese. Cobalt-base alloys were annealed at 800°C for 45 minutes in vacuum, but Mn-base alloys crumbled to powder on annealing at 800°C. The Mn-base alloys were kept at 350-400°C for 90 minutes in vacuum. The pattern still showed peak broadening, hence accurate angle measurements could not be done. Similarly the hardness measurements could not be carried out for Mn-base alloys because of thickness limitation (6–8 μm). Table-III gives the x-ray structure and microhardness of Co-base alloys.

TABLE—III X-ray structure and Hardness Values of Cobalt-base Alloys

Sl. No.	Bath No.	%Mn in the deposit	Conditions of Deposition	X-ray structure*	VHN**
1	II	4.4	pH = 3, 25°C, 8 A/dm²	f.c.c. Co	
2	-do-	5.2	-do-, 16 A/dm²	f.c.c. Co	467

3	III	4.0	pH=3, 50°C, 8 A/dm²	f.c.c. Co	227
4	-do-	5.1	-do-, 16 A/dm²		245
5	VII	12.8	pH-3, 25°C, 6 A/dm²	f.c.c. Co	
	Pure Mn***		-do-, 8 A/dm²	σ-Mn	

*Annealed, ** As deposited, *** As deposited from bath containing 16 gpl Mn, 110 gpl NH_4BF_4, 2 gpl $NH_2OH.HCl$, 0.5 gpl NH_4SeO_4, 35 gpl glycine and 0 1 gpl sodium lauryl sulphate ; 20 gpl sodium citrate added to the anolyte.

CONCLUSION

Optmium electrodeposits of Co-Mn alloy are obtained from fluoborate solutions containing 80 wt.% Mn along with 110 g/l ammonium fluoborate, 35 g/l glycine, 2 g/l hydroxylamine hydrochloride and 0.5 g/l ammonium selenate (Bath VI) operated at pH 3 and temperature 25°C and C.D. 16-40 A/dm². Addition of sodium lauryl sulphate is necessary to avoid pitting. Smooth, adherent, steel grey : cobalt-manganese deposits could be plated in the C. D. range of 2-40 A/dm² with 30 gpl citric acid addition. But it was not possible to electroplate deposits thicker than 6-8 μm from these baths. 20 wt.% Mn bath gives best results at pH = 3, 50°C and in the C.D. range of 4-20 A/dm² and alloy thicknesses upto 1 mil could be easily deposited. At intermediate composition baths (40, 50 and 60 wt.% Mn) neither good coatings nor intermediate alloy composition was obtained. The current efficiency of alloy deposition is low. Detailed studies are needed with special emphasis on maintaining the constant pH at cathode/solution interface, along with suitable stress relieving agents so that crack-free thick coatings could be obtained.

The results are based on laboratory studies and will require careful control of process variables for commercial application.

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