ALLOY PLATING : CODEPOSITION OF NICKEL - COBALT ALLOYS FROM FLUOROBORATE BATH

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The Electrodeposition of nickel-cobalt alloys from fluoroborate bath was investigated over a wide range of current density, temperature, pH, bath composition and agitation The optimum conditions for plating were arrived at as : $Ni^{2+} + Co^{2+}$, iM (individual concentration adjusted to get desired alloy composition); pH 2.5 to 3 5; temp. 25° to 50°C; c.d., 6 to 30 asd The superimposition of a c. over d.c. was favourable. The deposits were fine-grained and hard, and the deposition could be carried out at high current densities. The high rates of plating and the insensitivity of current efficiency, deposit nature and composition to variations of the plating parameters under optimum operating conditions have been pointed out to be of particular interest to the practical plater. Data from two laboratories are compared to create confidence in alloy plating amongst practical platers.

Nickel and Cobalt occupy a unique position among the important ferromagnetic metals. Although nickel plating is extensively used for decorative and protective purposes, cobalt remained a plating curiosity.

Alloy plating in general has received considerable attention in recent years[1]. There are reports of the industrial use of Ni-Co alloy deposits because of their brightness and hardness[2]. Alloys of Ni with Co have properties superior to Ni deposits[3]. Alloys of Ni with low Co content (up to 5%) are used in bright plating, while high-Cobalt deposits (25 to 45%) find application in protective finishing. A deposit with 40% Co has been used as a bright, white undercoat for Cr and Rh plate[4]. These alloys are stated to have some advantages for finishing magnesium alloys[5]. They have been electroformed for moulds and dies[6] and structural applications[7]. A 50-50 Ni-Co alloy has unique properties and should be of special interest for engineering applications because of their mechanical and magnetic properties[2] Numerous aerospace components such as waveguides, jet engine ducts, reflectors, venturi nozeles, rocket engine thrust chambers and vanes have been successfully produced by electroformed Ni-Co alloy deposits[7 9].

Recent applications of these alloys are in memory storage for computers[10 12]. Ni Co alloys obtained from sulfamate bath have coercive force as high as 500 oe[13 15]. Such coatings are said to possess recording properties superior to those of iron oxide coatings

The solutions that have been used for the plating of Ni-Co alloys are sulfate[16,17], chloride[17,19], sulfate-chloride[20,21], sulfamate[6,25], hypophosphite[26], triethanolamine[14], and ammoniacal pyrophosphate[27]. Industrial plating appears to be restricted to the sulfate-chloride type bath[24,28].

THE FLUOROBORATE BATH

Electrodeposition from the fluoroborate bath, more popularly known as the fluoborate bath, remained comparatively obscure except for the plating of lead[29] and later tin, cadmium, zinc, copper, iron, nickel, cobalt etc., when fluoroborate solution concentrates were available[30,31]. Now-a-days, the fluoroborate bath is widely used for decorative plating and also for producing coatings for engineering and electronic applications[32] and alloy plating[33,37]. Iron-group metals and alloys have been plated from fluoroborate baths[38,41], and Gover and Balachandra have reported that nickel-cobalt alloys could be deposited from boric acid-buffered fluoroborate bath at a current efficiency as high as 99%[42].

It has thus been established that the fluoroborate bath can be safely and easily employed for the deposition of a variety of alloys; but, it is doubtful whether the fluoroborate bath is ever used commercially for alloy plating. One of the reasons for this would be the apprehension regarding the reproducibility of the results from such baths, particularly with regard to alloy composition. The present work was undertaken to check this aspect with respect to nickel-cobalt alloys which has already been studied by Grover and Balachandra[42].

EXPERIMENTAL

The fluoroboric acid was prepared by saturating ice-cooled hydrofluoric acid with boric acid in a polythene vessel; after a minimum time of 36 hours, the excess of boric acid was filtered off and the resulting solution (4.5 to 5M with respect to HBF_4) was saturated with either nickel or cobalt carbonate. The solution was heated to drive off any dissolved carbon dioxide

and maintained at the crystallisation point in a water bath, filtered again and stored in glass containers which were found to be unaffected for months together. However, fluoroboric acid was stored in polythene containers since it attacked glass producing a permanent opalescence on long keeping. The solutions were analysed for their metal content by EDTA titration with xylenol orange and murexide as indicators for cobalt and nickel respectively.

The pH adjustments were made by the addition of fluoroboric acid or ammonia. The pH was measured using a glass electrode dipped for only a few seconds in the bath and withdrawn and washed immediately. A boric acid-saturated solution gave a pH in the range 2.8 to 3.2, which remained substantially constant for about a month, while an un-buffered solution changed by one pH unit. The total metal content of the bath was fixed at 1 molar, unless otherwise stated.

The bath volume was 150 ml in a 250 ml beaker placed in a thermostat. A cylindrical platinum cathode and a concentric platinum gauze anode were used, the interelectrode distance being 2 cms. The cathode was slipped on to a stainless steel holder and plugged at the bottom to prevent contact of the holder with the solution; the cathode assembly could be rotated, when necessary. A lead accumulater was used as the source of power. Polarization measurements were made in the usual manner.

Reduction of stress in deposits by superimposing A.C. on D.C. during plating is well known; the Marchese technique[43] was employed for this purpose.

The deposits were generally 10 to 12 microns thick. For hardness and microstructure studies, the deposits were around 100 microns thick; they were deposited on rectangular copper plates from larger volumes (3 litres) of solutions so that the composition changes in the deposit composition was minimum.

On completion of plating, the deposit was stripped in hot nitric acid and analysed complexometrically: total nickel+cobalt by back titration of excess EDTA with calcium to the Calcein end point, and nickel alone by the Pribil-Vesely method[44].

RESULTS AND DISCUSSION

There was a slight decrease in pH of the used solution with time. The deposits from these aged solutions had higher nickel contents and were in many respects better than the deposits from a freshly prepared solution.

Effect of bath Composition : Keeping the total metal concentration at 1.0 M at 30°C, 3.4pH and still plating, the nickel concentration in the bath was varied from 0.1 to 0.95M. The nickel content in the deposit presented in Fig. 1, lies below the composition

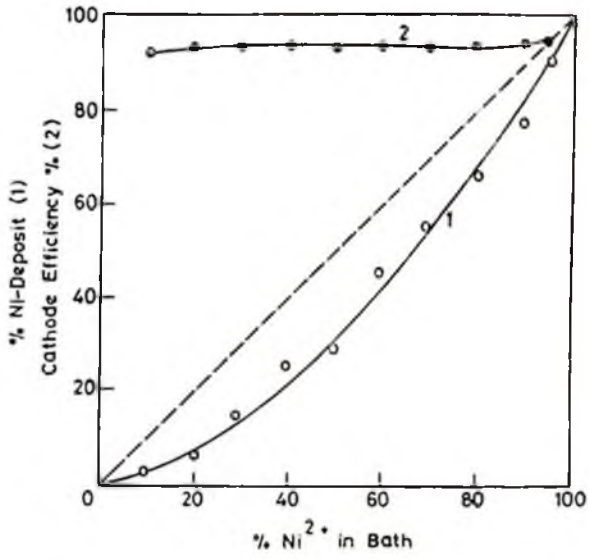


Fig. 1 Effect of bath composition ($Co^{2+} + Ni^{2+}$ = 1M; 30°C; pH3.4; 10 asd).

reference line, thus indicating that nickel is the less readily deposited metal; an exactly similar observation has been made by Grover and Balachandra[42] It is a well-known fact that the iron group metals exhibit the phenomenon of anomalous codeposition[38,41]. We observed that the cathode efficiency remains constant at 95% in the entire composition range while Grover and Balachandra[42] report that the efficiency is only around 80% in high-cobalt baths

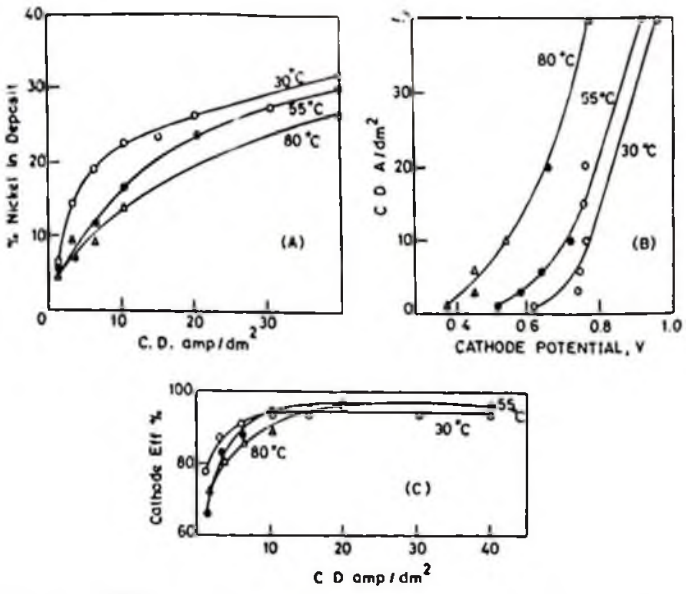


Fig. 2 Effect of C D and temperature (0.6 M Ni^{2+} + 0.4 M Co^{2+}; p H 3.4; still)

Effect of Temperature and Current Density : The nickel content of the deposit decreases, though slightly, with temperature, but current efficiency remains practically constant with current density up to 40 asd, except at low current densities (2 to 10 asd) (Fig. 2). The effect in probably due to the fact that higher temperatures decrease polarization and increase diffusion processes, particularly of cobalt. The deposits were smooth and of less stressed at 25° to 50°C, but not at higher temperatures and lower current densities.

Effect of pH : Most of the investigators[1,4,2,1] have noticed that the nickel content of the deposit increased slightly with pH (Fig. 3), more so at low current densities. In low pH baths, the current efficiency is low at low current densities, but it is fairly constant and high at high current densities. The best pH to operate was around 3.0, which is the pH of the boric acid-saturated solution.

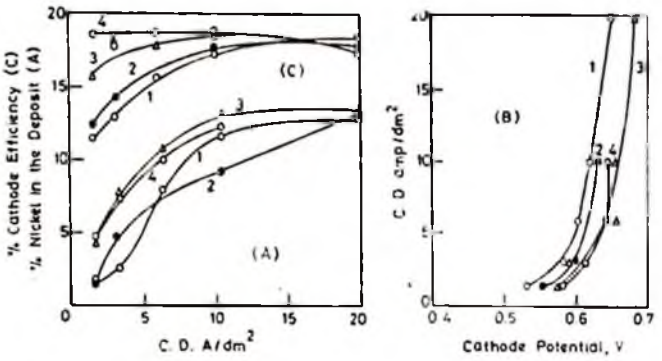


Fig 3 Effect of pH (0.8 M Ni^{2+} + 0.2 M Co^{2+}, 30°C, still) pH = 2.3(1); 2.8(2); 4.5(3); 5.0(4).

Effect of Agitation : The nickel content as well as the cathode current efficiency decreases with cathode agitation (Fig.4). The effect is more pronounced at low current densities. Considerable deterioration was observed in the nature, appearance and stress of the deposits when the cathode was rotated. As far as practical plating is concerned, agitation is unnecessary (vide infra)

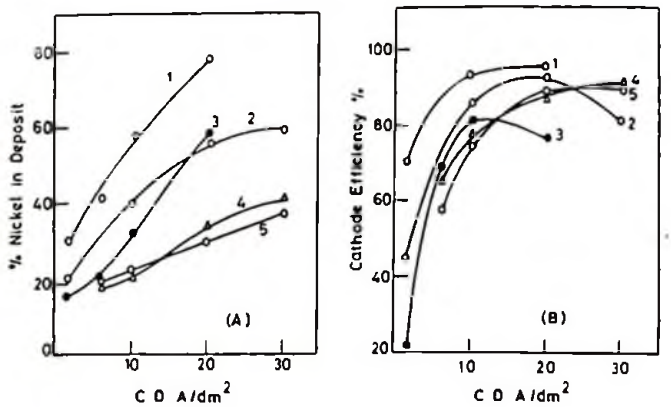


Fig. 4 Effect of agitation (0.8 M Ni^{2+} + 0.2 M Co^{2+}, pH 3, 30°C) rpm – 0(1); 140(2); 350(3); 570(4); 870(5).

Effect of Superimposition of AC on DC : By the superimposition of AC over DC, the bath gets heated up above the AC to DC ratio of 1.5, sometimes as much as 10°C. Fig. 5 shows that superimposition of AC over DC increases the nickel content and cathode efficiency if the bath is agitated; otherwise, the effect is negligible. And, AC superimposition gives the best deposits with bright shine when the cathode was rotated

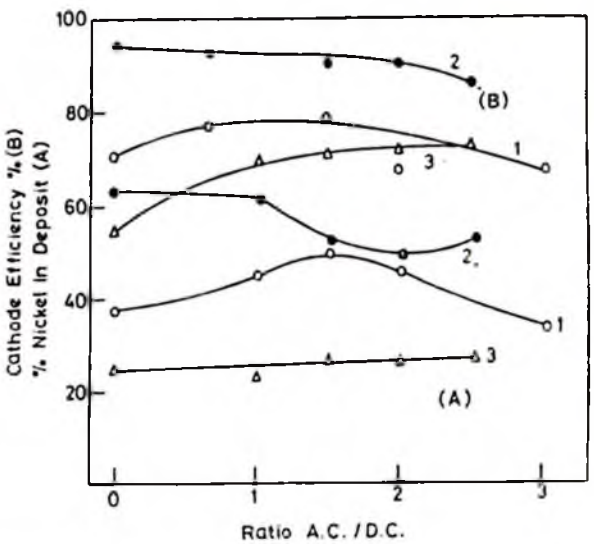


Fig. 5 Effect of AC superimposition (0.8 M Ni^{2+} + 0.2 M Co^{2+}) (1) pH 3.1, 2.5 asd, still; (2) pH 5.0, 5.0 asd, still; (3) pH 4.9, 5 asd, 140 rpm.

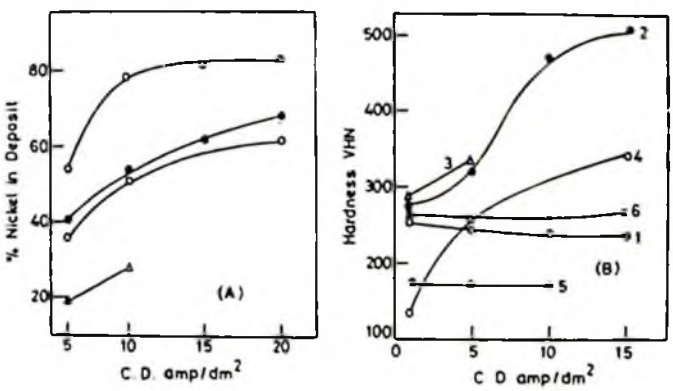


Fig.6 Effect on (A) Composition, (B) hardness Total metal conc. 59.0 gpl (1) Ni^{2+} 48.7 gpl, pH 3.0, 30°C; (2) Ni^{2+} 39.0 gpl, pH 2.9, 30°C; ( ) Ni^{2+} 47.0 gpl, pH 3.1, 80°C; (4) Ni^{2+} 41.0 gpl, pH 4.0, 30°C; (5) Ni^{2+} 20 gpl, pH 3.1, 30°C; (6) Ni^{2+} 59.0 gpl, pH 3.0, 30°C.

in a high pH bath; this is important if we recollect that neither cathode rotation nor high pH was favourable when there was no AC superimposition.

Hardness of the Deposits : The hardness of the alloy deposits are compared with those of nickel as well as cobalt in Fig. 6. Temperature, pH and current density have considerable effect on hardness. The hardness of an alloy deposit obtained at a pH of 4 at 6 asd is less than that of pure cobalt deposit. The hardness from low cobalt-high nickel bath is less than that of pure nickel deposit. Some of the deposits possessed hardness as high as 500 VHN.

Microstructure : The deposits were all fine-grained, even those obtained at 80°C. Some of the deposits were laminar or banded in structure. The finer grain size may be the result of interference with crystal growth by codeposited metal hydroxides or hydrogen. The laminar structure of the alloys has been attributed to the cyclic adsorption or inclusion of impurities (eg. hydroxides) or addition agents; the layer may be a consequence of periodic fluctuations in the concentration of impurities or addition agents at the growing metal surface.

Optimum operating Conditions : Table 1 presents the effect of all variables on alloy deposition: nature of deposits, deposit composition, and cathode efficiency; and in the light of these, the optimum operating conditions are recommended. These are compared with those of Grover and Balachandra[42]. There is a striking similarity between the conclusions drawn from both the studies. This is important in that the practical plater need not be apprehensive of alloy plating baths, in particular the fluoroborate bath for nickel-cobalt alloy deposition. The bath gave adherent, bright and smooth alloy deposits of any composition, the color ranging from dull grey to bright platinum shine, depending on plating variables. It was possible to obtain alloys of any composition by changing nickel-to-cobalt ratio in the bath, which was found to be more effective than other variables. The bath was quite stable, even though aged baths were found to give more adherent and bright deposits than the freshly prepared baths.

Table 1. Effect of variables and optimum operating conditions.

No.	Variable	%Ni in Deposit	Cathode Efficiency	Optimum Operating Conditions	
				Present Study	Grover & Balachandra (Ref 42)
1	Total Metal Concentration	—	—	1M; boric acid saturated	1 to 2M; 20–40 gpl boric acid
2	Increase in Ni^{2+} Conc. in bath	Increase	No Appreciable change	Effective variable to get the desired alloy composition	Effective variable to change deposit composition
3	Increase in current density	Increase	Increase	Good deposit at 6 to 30 asd	Good deposit at 4 to 12 asd
4	Increase in temperature	Slight Decrease	Slight decrease at low c.d.	25° to 50°C	25°C
5	Increase in pH	Slight Increase	Increase	Around 2.5 to 3.5 (boric acid sat)	Around 2.5
6	Agitation	Decrease Stressed deposit	Decrease	Still Plating	Still Plating
7	Anode	—	—	Insoluble or Platinum Anode	Alloy Anode or Platinum
8	Superimposition of AC	Slight Increase	Slight Increase	Useful; best deposit at the AC to DC ratio of 1 to 2	—

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