FLUOBORATE BATH FOR THE PLATING OF THE TERNARY ALLOY: IRON-COBALT-NICKEL

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ABSTRACT

Plating of the ternary alloy, iron-cobalt-nickel, has been effected from the fluoborate bath; anomalous codeposition has been observed. The effect of metal ion concentration, temperature, pH and agitation on the metal content of the deposit has been studied. Optimum conditions for plating a cobalt-and a nickel-rich alloy are given.

Introductory

The ternary iron-cobalt-nickel alloy evinced interest in the past because of its potential applicability in glass-to-metal seals. Today, with the advent of various memory storage devices, the interest in this alloy has increased several fold. The electro-deposition of the ternary iron-cobalt-nickel alloy has been patented[1-9] for use in memory storage devices. Recent work[10] has shown that evaporated thin films of nominal composition close to 60% Ni, 25% Fe and 15% Co, are found to meet the sonic film memory requirements with respect to their magnetic and magnetostrictive properties. Also, these alloys are claimed to have resistance towards gaseous and humid media[11].

Despite these interesting applications of this ternary alloy, attempts towards electrodepositing it have been limited. Deposition has been carried out from the sulphate 1, 2, 12-14, sulphate-chloride 3–7, 11, 15, 16alkaline[17], citrate[8] and sulphamate[18] baths; but most of the work is covered by patents and hence detailed information on the effect of the different variables is not available. Recent work in the pyrophosphate bath[19] provides some insight into the deposition characteristics of the alloy from a complex bath.

Experimental

Previous work done in these laboratories[20] on the electrodeposition of iron, cobalt and nickel from the fluoborate bath suggested the possibility of obtaining the ternary alloy from this bath. The total metal concentration was kept at one mole per litre since the observations during single metal deposition pointed to optimum conditions at that concentration. Fluoborate solutions of the metals were prepared by saturating fluoboric acid with the appropriate metal carbonate and evaporating the solution to saturation. The different solutions were mixed in the required ratio and saturated with boric acid shortly before the deposition; the pH was adjusted using fluoboric acid or ammonia.

The experimental set up used for deposition and the simultaneous measurement of the cathode potential has been described elsewhere[20]. The cylindrical cathode could be rotated when necessary. The period of deposition was adjusted so that the thickness of the deposit was around ten microns. The deposited ternary alloy was stripped from the platinum electrode using acid and analysed, following on EDTA technique[21] employing Pb^{2+} and Ca^{2+} as titrants and Xylenol orange and calcein as indicators. The cathodic current efficiency was calculated from the partial efficiencies.

Results and Discussion

The data obtained on the influence of the metal ion concentration in the bath on the composition of the alloy deposit showed that cobalt and iron deposited preferentially to nickel although, of the three metals, nickel has the highest standard electrode potential. This phenomenon of anomalous codeposition was observed in the entire range of concentration,

temperature and pH investigated. Hence, nickel-rich deposits were obtainable only when the nickel ion concentration in the bath was more than 6 times that of iron or cobalt. Fig. 1 gives the variation of composition of the deposit when the metal ion concentration of one of the species in solution is kept constant and the ratio of the other two is varied. From Fig. 1c it is seen that the variation of the ferrous to cobalt ion ratio in solution has little effect on the nickel content of the deposit. This was true for various concentrations of nickel (20 to 60% in solution) investigated. Also, theiron to cobalt ratio in solution and in the deposit are not much different. Fig. 1b shows that the alteration in the ratio of cobalt to nickel ion concentration in solution does not affect the percentage of iron in the deposit considerably although this was not the case when the ferrous ion concentration was higher than that shown in the figure. Figure 1a shows no such regularities in behaviour, and is in conformity with the results in the sulphate-chloride bath[15]. Nickel-rich and cobalt-rich deposits (ie., above 60% of the metal) were bright, smooth and adherent wheres iron-rich ones were invariably dark and brittle.

The effect of the variation of the current density was studied inbaths of various compositions. Fig. 2 gives the results obtained using a bath meant to give nickel-rich deposits Increasing the current density from 0 to 10 amps. dm^{-2}. is found to increase the total efficiency of deposition as well as the nickel content of the deposit; this is accompanied by a general decrease in the iron and cobalt content. Further increase of the current density to 25 amps.dm^{-2}. results in little change in the composition of the deposit. In fact, a bright and silvery alloy deposit at 92 per cent efficiency is obtainable even at 36 amps.dm-2. Solutions meant to yield cobalt-rich deposits could also be operated with high efficiency at current densities up to 36 amps.dm^2. and conformed to the same trends of behaviour. In the case of solutions yielding deposits rich in iron, however, the compositional changes were practically nil, although the efficiency increased with current density.

Temperature changes of the bath did not have considerable effect on the efficiency of deposition or the metal content of the deposits, although there was a steady decrease in polarization with increasing temperature. The deposits obtained at room temperature were found to be highly stressed and peeled, and hence operation at 40°C. was adopted for the rest of the investigation.

Increasing the pH of the bath improved the current efficiency of deposition and increased the nickel content of the deposit. At current densities of 6 amps.dm^{-2}. and below, a low pH was favourable since the alloy produced had a better physical appearance. At pH values of 4 and above, the deposits obtained were dull and highly stressed.

Rotation of the cathode during deposition was found to be unfavourable since it produced undesirable effects on the nature of the deposits obtained. Fig. 3 shows that the current efficiency as well as the nickel content of the deposit decreases with increase in the speed of rotation of the cathode; the iron and cobalt content increases, the former being more considerable.

The optimum conditions for plating a cabolt rich and a nickel-rich deposit are given in Table 1

TABLE 1

OPERATING CONDITIONS FOR THE DEPOSITION OF IRON-COBALT-NICKEL TERNARY ALLOYS FROM THE FLUBORATE BATH

Variable	*Cobalt-rich alloy*	*Nickel-rich alloy*
bath composition, moles/ litre		
iron ...	0.125	0.05
cobalt ...	0.375	0.50
nickel	0.500	0.09
boric acid	to saturation	to saturation
temperature, °C	40 to 60	40 to 60
pH ...	2 to 3	2 to 3
agitation, r.p.m.	nil	nil
current density, amps.dm-2 ...	10 to 30	15 to 30
cathode efficiency, % ...	90 to 95	90 to 95
alloy composition, et. %		
iron	15 to 20	5 to 10
cobalt ...	40 to 50	8 to 12
nickel ...	30 to 40	78 to 87

Detailed investigations on the influence of the plating variables and the effect of various addition agents on the polarization and microstructure are in progress.

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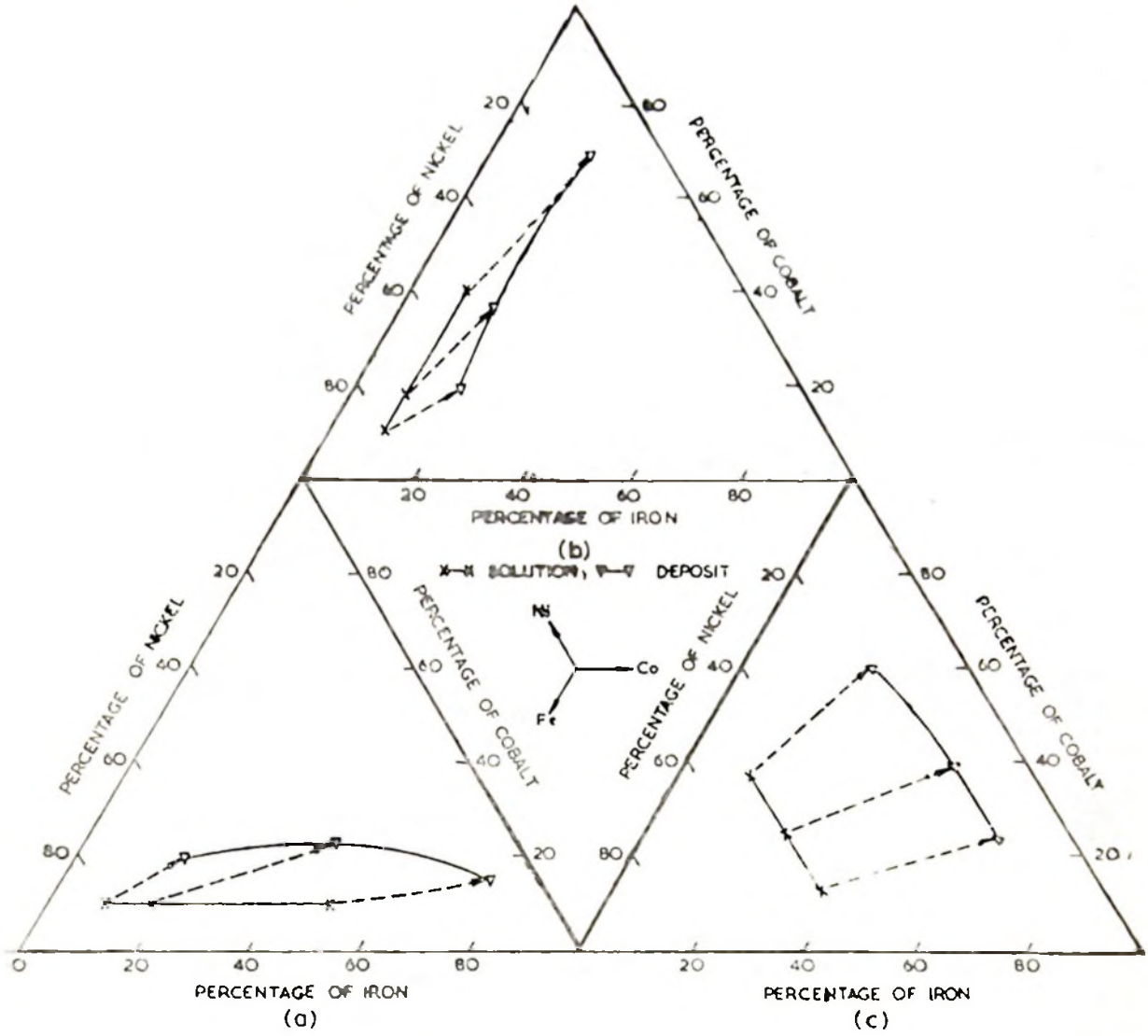


Fig. 1. Effect of metal ion concentration in solution on the metal content in the deposit. (a) 0.1M Co^{++}; 0.9M (Fe^{++}+ Ni^{++}); Ni^{++}/Fe^{++} ratio: 8, 4, 4/5; 40°C; pH 2.5; 10 amps.dm.$^{-2}$; still plating. (b) 0.1M Fe^{++}; 0.9M (Co^{++}+ Ni^{++}); Ni^{++}/Co^{++} ratio: 8, 4, 4/5; 40°C; pH 2.5; 10 amps.dm.$^{-2}$; still plating. (c) 0.5M Ni^{++}; 0.5M (Fe^{++}+ Co^{++}); Co^{++}/Fe^{++} ratio: 3, 1, 1/3; 40°C; pH 2.5; 10 amps.dm.$^{-2}$; still plating.

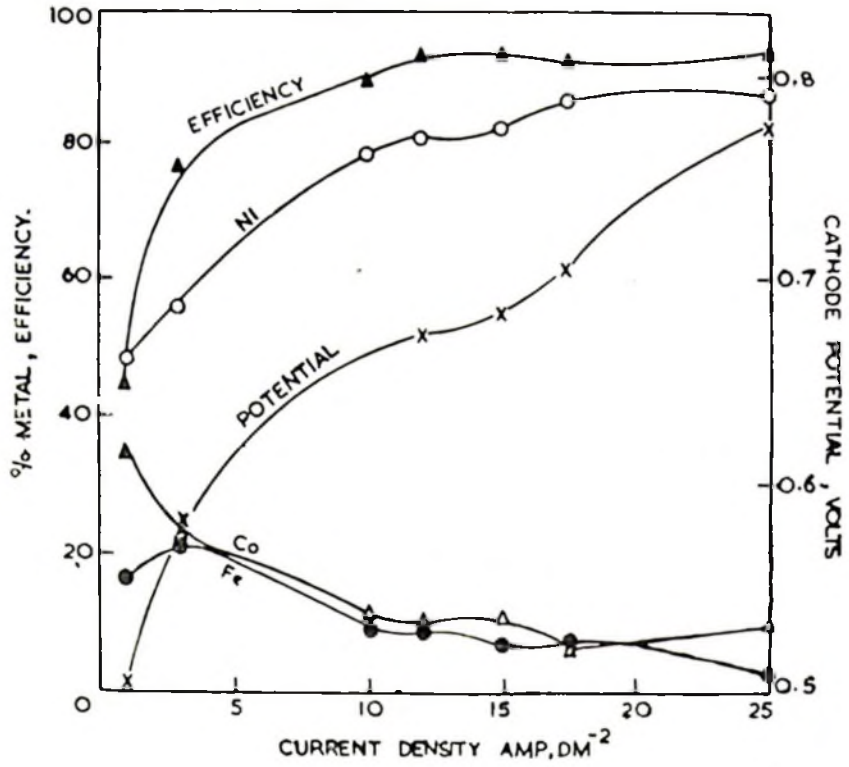


Fig. 2. Effect of current density on the cathode current efficiency cathode potential and deposit composition.
0.05M Fe++, 0.05M Co++ and 0.90M Ni++; 40°C; pH 2.65; still plating.

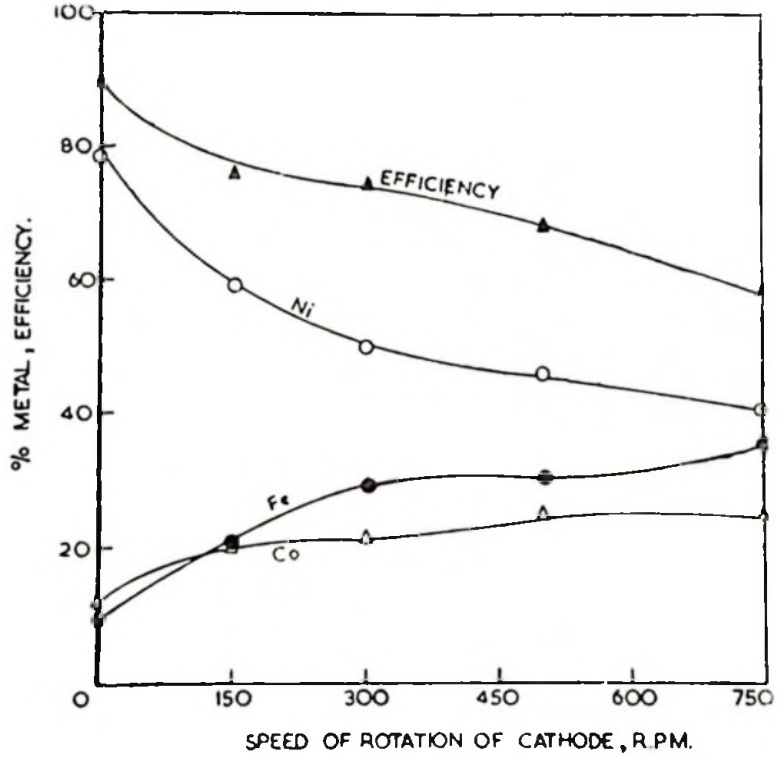


Fig. 3. Effect of agitation on the cathode current efficiency and deposit composition.
0.05M Fe++, 0.05M Co++ and 0.90M Ni++; 40°C; pH 2.65; 10 amps.dm.$^{-2}$

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