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The electrodeposition of cobalt–molybdenum alloys

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Previous studies have shown that cobalt–molybdenum alloys may be deposited with high efficiencies from a pyrophosphate bath using a specially designed plating cell incorporating cathode rotation, stirring and wiping. This investigation shows that it is possible to deposit bright and adherent alloys using a pulsed-potential method in the same bath, even without stirring, wiping or cathode rotation. The average content of the deposits was about 55 % molybdenum, 40 % cobalt and 5 % non-metallic material. The cathode current efficiency was about 47 %.

1. Introduction

The codeposition of molybdenum with iron, cobalt, nickel, copper and zinc from pyrophosphate baths has been studied extensively by Myers [1]. Further investigation on the codeposition of molybdenum–iron alloys from the same bath was carried out by Case and Krohn [2] and the deposition of cobalt–molybdenum alloys by Krohn and Brown [3]. The main innovation of Krohn and his co-workers was the introduction of cathode rotation, and wiping and stirring of the solution. This is the main reason why the efficiencies reported by Krohn and his co-workers increased up to 45 % from about 10 or 20 % as reported by Myers [1].

This paper describes the results of the pulsed potential technique for the deposition of cobalt–molybdenum alloys. The effect of frequency, effective current density and the length of plating time on the current efficiencies and deposit composition is reported.

2. Experimental details

2.1. Apparatus

The plating cell consisted of a cylindrical platinum anode and a cylindrical copper cathode. The cylindrical geometry resulted in a more symmetrical current distribution than with flat electrodes. Potentiostat type PRT 20-2x connected to a PAR-universal programme, model 175, were used.

2.2. Plating bath

The bath used in this investigation was essentially the same as the one used by Myers [1], modified by the addition of hydrazine sulphate to prevent the oxidation of Co(II) to Co(III) at the anode.

The plating solution had the following composition: 33.6 g dm^{-3} $Na_2MoO_4 \cdot 2H_2O$; 8.1 g dm^{-3} $CoCl_2 \cdot 6H_2O$; 80 g dm^{-3} $NaHCO_3$; 60.0 g dm^{-3} $Na_4P_2O_7 \cdot 10H_2O$ and 1.5 dm^{-3} $N_2H_4 \cdot H_2SO_4$. The temperature of the plating bath was maintained at 60° C.

2.3. Analyses of the deposits

The alloy deposits were washed, dried, weighed and dissolved from the cathode in 5 N nitric acid. The molybdenum and cobalt were analysed by atomic absorption spectroscopy.

3. Experimental results

Most of the plating runs were for 20 min at 10^4 Hz. The potential time profile used in this work was a repetitive square wave [4–7]. The deposits were found to contain about 5 % non-metallic material (NMM) which may have been oxygen [1, 2], hydrogen [8, 9], or both. The percentage of NMM was obtained by subtracting the total percentage of molybdenum and cobalt from 100. The calculation of the cathode current efficiency (CCE) assumed that the oxidation states of molybdenum and cobalt in solution to be (VI) and (II), respec-

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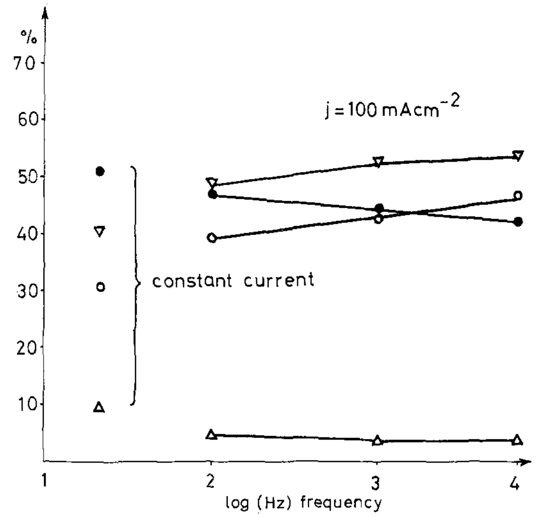

Fig. 1. The effect of pulsed-potential frequency. (•) % Co; (▾) % Mo; (△) % NMM; (○) % CCE.

tively. The effects of changes in plating conditions on the deposits and cathode current efficiency are summarized by the following graphs and discussion. When conditions were found to be better than those used previously, these were retained for the remainder of the investigation.

3.1. Effect of frequency

Runs were carried out at frequencies varying from 10^2 to 10^4 Hz. The length of each plating run was adjusted so that a total of 60 C had passed at an effective current density of 100 mA cm^{-2}. The deposits obtained at a constant overpotential were almost black in appearance, thin and not very adherent. The molybdenum content was low, and the cobalt and non-metallic material content was high.

As the frequency of the potential pulse was increased, the deposits became more adherent and the molybdenum content as well as the current efficiency became higher (Fig. 1).

3.2. Effect of current density

The potential was varied so that the effective current density ranged from 25 to 400 mA cm^{-2} at a frequency of 10^4 Hz. The deposits at low current densities were metallic steel grey colour. At extremely high current densities, the colour of the deposits changed to a light grey and the efficiency decreased (Fig. 2a–d).

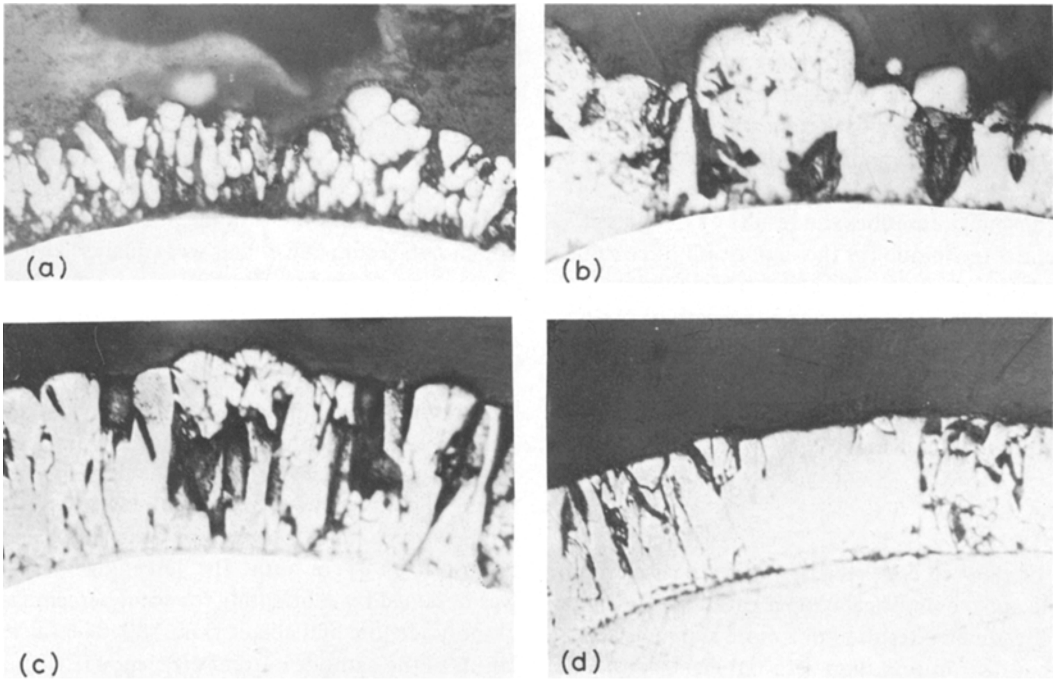

Fig. 2. Microphotographs of cobalt–molybdenum (X 250). τ = 90 min; ν = 10^4 Hz. (a) 400 mA cm^{-2}; (b) 200 mA cm^{-2}; (c) 50 mA cm^{2}; (d) 25 mA cm^{-2}.

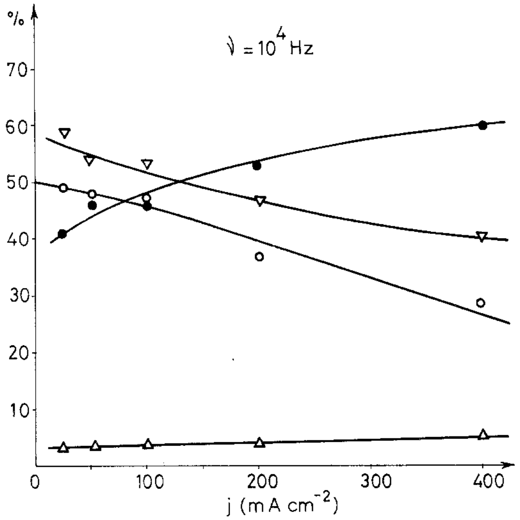

Fig. 3. The effect of the effective current density. (●) % Co; (▽) % Mo; (△) % NMM; (○) % CCE.

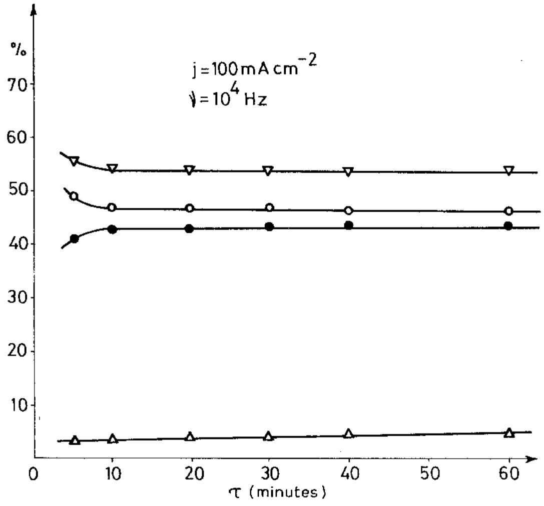

Fig. 4. The effect of plating time. (●) % Co; (▽) % Mo; (△%) NMM; (○) % CCE.

Both the molybdenum content and the current efficiency were greater at low current densities than at high current densities (Fig. 3). Good deposits with high efficiency and high molybdenum content were obtained at current densities ranging from 25 to 150 mA cm^{-2}.

3.3. Effect of plating time

Runs of 5 to 19 min were carried out. The composition of the deposits obtained at an effective current density of 100 mA cm^{-2} varied only slightly as shown in Fig. 4. As the plating time was increased, the deposits became greyish and less adherent, especially at higher current densities (Fig. 5a–d). The efficiency decreased continuously as the plating time was increased.

4. Summary and conclusion

The primary purpose of this investigation was to obtain a deposit with a high molybdenum

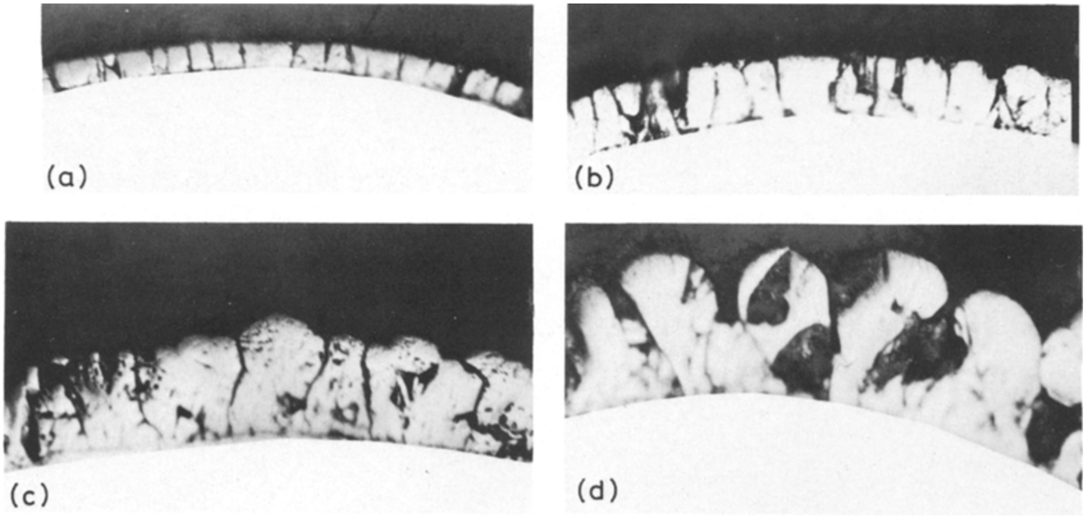

Fig. 5. Microphotographs of cobalt–molybdenum (× 250). j = 100 mA cm^{-2}; $\nu = 10^4$ Hz. (a) τ = 20 min; (b) 40 min; (c) 60 min; (d) 90 min.

content and a high current efficiency. These results show that it is possible to deposit bright and adherent alloys with high molybdenum contents and high current efficiency using a pulsed-potential technique in a bath without any cathode rotation, stirring or wiping.

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