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Electrodeposition of cobalt–nickel alloys from Watts-type baths

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The electrodeposition of cobalt–nickel alloys was carried out from Watts-type baths of composition 5–60 g l^{-1} $CoSO_4 \cdot 7H_2O$, 100–300 g l^{-1} $NiCl_2 \cdot 6H_2O$ and 25 g l^{-1} H_3BO_3 at a pH of 4.4. The cathodic polarization during electrodeposition and the alloy composition were greatly influenced by the concentrations of the depositable metal ions; whereas, the cathodic efficiency was only slightly affected. Under the examined conditions, the electrodeposition of the alloys belonged to the anomalous type. X-ray diffraction studies revealed that the alloys were deposited in the face-centred cubic structure and consisted of a mixture of the two phases α(Co) and β(Ni). Sound, smooth and bright alloy deposits were obtained and their properties were improved by increasing the nickel content of the bath.

1. Introduction

Electrodeposition of cobalt–nickel alloys is of practical importance because the alloys have high protective and decorative values, besides a wide range of industrial applications. As an example, the alloy is used in the electroforming of moulds for die-casting and plastics [1] and in electrotyping [2]. The magnetic properties of the cobalt–nickel alloy are of interest in electronic applications such as memory drums, discs, cards and tapes particularly in the computer industry [3, 4].

Recently, comprehensive studies have been carried out on the electrodeposition of cobalt–nickel alloys from simple and complex-ion baths. The simple baths include chloride [5], sulphate [6, 7] and sulphamate [8, 9] solutions. However, insufficient research was carried out on the deposition of the alloy from simple sulphate–chloride baths (Watts-type) baths.

Accordingly, we felt it would be interesting to investigate the effect of the bath constituents on the characteristics of the cobalt–nickel alloy deposition from Watts-type baths. Such a study is expected to provide additional quantitative data concerning the Watts bath composition required to electrodeposit an alloy of predetermined composition and, hence, properties.

2. Experimental details

The deposition baths were freshly prepared in distilled water using highly pure chemicals (BDH); their symbols, numbers and compositions are given in Table 1. The pH of each bath was 4.4.

The experimental set-up for the electrodeposition process consisted of a Perspex cell fitted with a copper cathode and two plane-parallel anodes. The cathode was positioned midway between the anodes and the cell was filled with the appropriate solution. The cathode and both anodes were of equal area. In cobalt and cobalt–nickel alloy deposition, the anodes were surrounded by asbestos diaphragms to preclude oxidation of Co^{2+} ions and errors in the measured potentials caused by the oxygen evolved at the anodes.

The cathodic potentials were measured relative to the saturated calomel electrode (SCE) and the efficiency was determined coulometrically. The composition of each deposited alloy was determined by means of an atomic absorption spectrophotometer (Unicam SP 1900). The morphology of the as-formed deposits was examined with a scanning electron microscope (JEOL Model JSM 35). X-ray diffraction analysis of the cobalt–nickel alloys was carried out using a Philips diffractometer (30 kV, 20 mA) with an iron filter and cobalt radiation.

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Table 1. Composition of cobalt, nickel and cobalt–nickel alloy deposition baths

Bath number	*Concentration of bath constituents* ($g\,l^{-1}$)			
	$CoSO_4 \cdot 7H_2O$	$NiCl_2 \cdot 6H_2O$	$NiSO_4 \cdot 6H_2O$	H_3BO_3
Co. 1	5	–	–	25
Co. 2	15	–	–	25
Co. 3	35	–	–	25
Co. 4	60	–	–	25
Ni. 1	–	100	–	25
Ni. 2	–	150	–	25
Ni. 3	–	200	–	25
Ni. 4	–	300	–	25
(Co–Ni) 1	5	200	–	25
(Co–Ni) 2	20	200	–	25
(Co–Ni) 3	35	200	–	25
(Co–Ni) 4	60	200	–	25
(Co–Ni) 5	35	100	–	25
(Co–Ni) 6	35	150	–	25
(Co–Ni) 7	35	300	–	25
(Co–Ni) 8	35	–	221	25

3. Results and discussion

3.1. *Polarization curves*

Cathodic polarization curves are helpful in providing useful information in the field of metal and alloy electrodeposition. This is due to the fact that the deposition potentials of the parent metals and the alloy affect the current efficiencies and provide an efficient way of predicting the possibility of codeposition, as well as determining the compositions of the electrodeposited alloys.

Figs. 1 and 2 show the cathodic polarization curves of individual cobalt and nickel deposition from baths Co. 1–4 and Ni. 1–4, respectively. The curves are characterized by a gradual increase of polarization with increasing deposition current density. Yannakopoulos and Brenner [10] concluded that in practical deposition from solutions of simple ions such a cathode polarization is mainly of the activation-type. Increasing the content of cobalt (Fig. 1) or nickel (Fig. 2) in the deposition baths causes a polarization decreasing-effect over the whole range of current density used. These effects could be attributed to the decrease in the concentration polarization [11]. A comparison between Figs. 1 and 2 shows that the

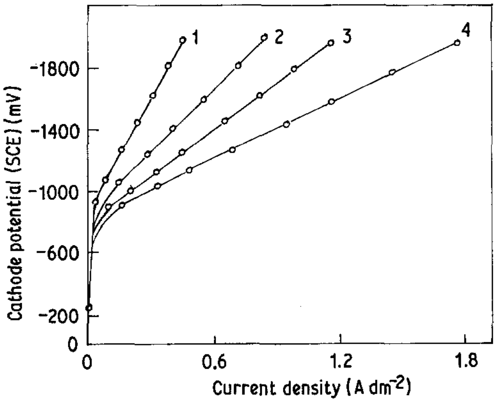

Fig. 1. Polarization curves for cobalt electrodeposition from baths Co. 1–4.

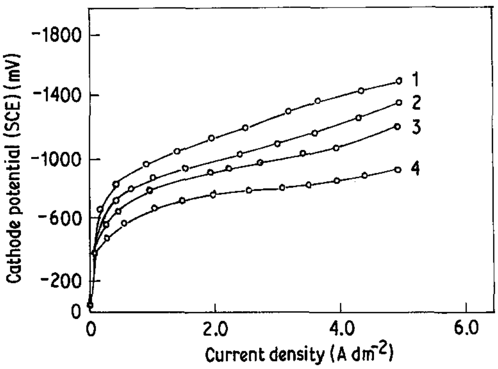

Fig. 2. Polarization curves for nickel electrodeposition from baths Ni. 1–4.

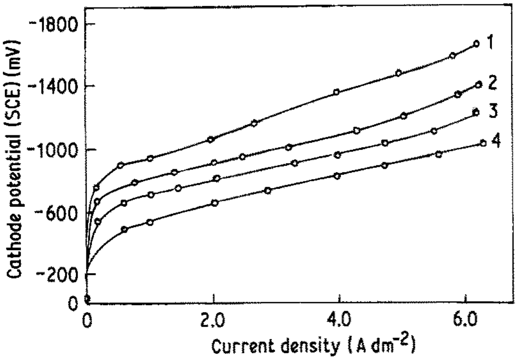

Fig. 3. Polarization curves for cobalt–nickel alloy electrodeposition from baths (Co–Ni) 1–4.

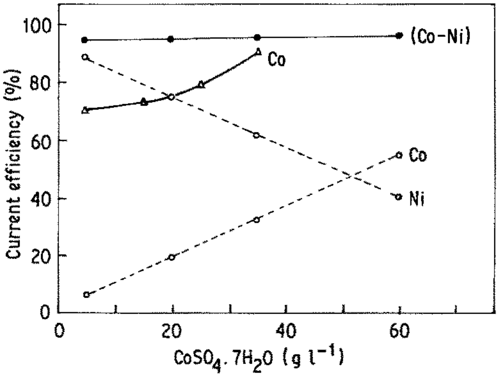

Fig. 5. Current efficiencies of cobalt from baths Co. 1–4, cobalt–nickel alloys from baths (Co–Ni) 1–4 and the partial efficiencies of cobalt and nickel in the alloys (broken lines). Plating time was 15 min at a current density of 1 A dm^{-2} for cobalt and 5 A dm^{-2} for the alloys.

electrodeposition of cobalt is attended by a greater polarization than nickel and this could be correlated to the low concentrations of Co^{2+} in the Co. 1–4 baths.

The data of Figs. 1 and 2 indicate that the static potentials of cobalt and nickel are about 200 mV apart and that the individual deposition of each metal is accompanied by a different overpotential. This means that the electrodeposition of a cobalt–nickel alloy is not an equilibrium process and will be governed by the operation of several factors. For this reason, the cathodic polarization curves of cobalt–nickel alloy deposition from the Watts (Co–Ni) 1–7 baths were recorded and the results are given in Figs. 3 and 4. Inspection of the curves of these figures shows, in general, that the cathodic polarization increases with increasing current density. Moreover, at a constant concentration of Ni^{2+} the cathodic polarization shifts to more noble values by increasing the concentration of Co^{2+} in baths (Co–Ni) 1–4 (see Fig. 3). Similar results are also observed for increasing the concentration of Ni^{2+} in baths (Co–Ni) 5, 6, 3 and 7 at a constant concentration of Co^{2+} (see Fig. 4). These results could be attributed to the decrease of the concentration polarization of the metal ion with increasing concentration in the bath [11].

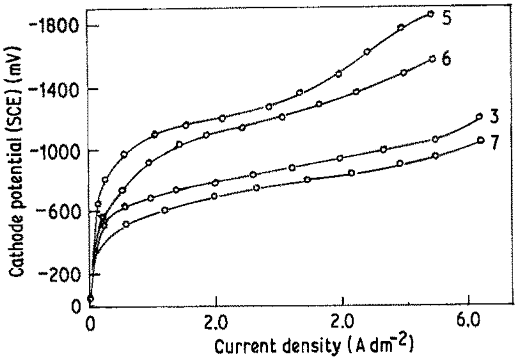

Fig. 4. Polarization curves for cobalt–nickel alloy electrodeposition from baths (Co–Ni) 5, 6, 3 and 7.

3.2. *Current efficiency*

The influence of increasing concentrations of Co^{2+} and Ni^{2+} on the percentage cathodic current efficiencies (*f*%) of the individual deposition of cobalt and nickel are illustrated in Figs. 5 and 6, respectively. The same figures show also the influ-

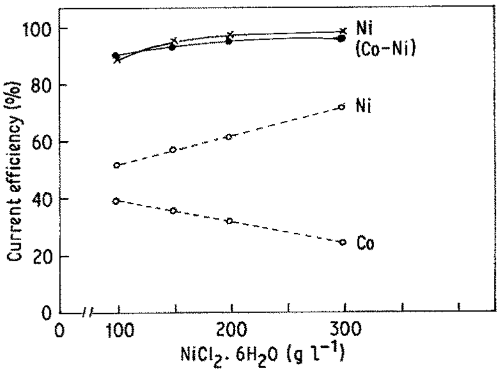

Fig. 6. Current efficiencies of nickel from baths Ni. 1–4, cobalt–nickel alloys from baths (Co–Ni) 5, 6, 3 and 7 and the partial efficiencies of cobalt and nickel in the alloys (broken lines). Plating time was 15 min at a current density of 3 A dm^{-2} for nickel and 5 A dm^{-2} for the alloys.

ence of the above-mentioned variables on the efficiency of the deposition of cobalt–nickel alloys and the partial efficiencies of both cobalt and nickel in each alloy (broken lines).

Inspection of Fig. 5 reveals that the *f*% of cobalt in individual deposition is relatively small, at a low concentration of Co^{2+}, and increases gradually with increasing concentration of Co^{2+} in baths Co. 1–4. This result could be ascribed to the fact that at a low concentration of Co^{2+} the electrodeposition of cobalt is attended by a large polarization term (see Fig. 1) and therefore, hydrogen is discharged preferentially resulting in a lower *f*% of cobalt deposition. However, on increasing the concentration of Co^{2+} the observed decrease of the concentration polarization (see Fig. 1) leads to an improvement of the *f*% of cobalt. Fig. 5 illustrates also that the increasing concentration of Co^{2+} in the alloy baths (Co–Ni) 1–4 has no significant effect on the *f*% of the alloy, whereas the partial *f*% of cobalt in the alloy increases at the expense of the partial *f*% of nickel which almost decreases in the same proportion.

Similarly, Fig. 6 shows that on increasing the concentration of Ni^{2+} in baths Ni. 1–4 and baths (Co–Ni) 5, 6, 3 and 7 there is correspondingly a slight increase of the *f*% of the individual nickel and the alloy deposition, respectively. However, each approaches a maximum efficiency of 100%. On the other hand, the partial *f*% of nickel in the alloy increases markedly and that of cobalt decreases sharply on increasing the concentration of Ni^{2+} in the alloy plating baths. These results could be explained on the basis that increasing the content of a metal ion in the bath increases its deposition efficiency through the corresponding decrease of the concentration polarization at the cathode [11].

3.3. *Composition of the alloy*

The effects of increasing concentrations of Co^{2+} in baths (Co–Ni) 1–4 and Ni^{2+} in baths (Co–Ni) 5, 6, 3 and 7 on the composition of the electrodeposited cobalt–nickel alloys were determined and the results are presented in Figs. 7 and 8, respectively.

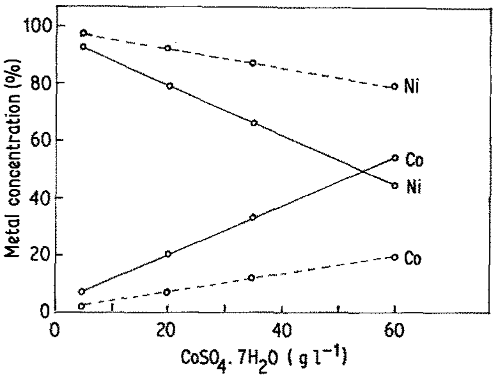

Fig. 7. The percentages of cobalt and nickel in the alloys deposited from baths (Co–Ni) 1–4 (solid lines). The broken lines represent the metal percentages in the alloy baths. Plating time was 15 min at a current density of 7 A dm^{-2}.

The outstanding feature of both figures is that the composition curve of the less noble metal in the alloy, cobalt, lies above its composition reference (broken line) which represents the Co % in the deposition baths, whereas the composition curve of nickel in the alloy lies below its composition reference (broken line). These data show that cobalt, the less noble metal, is preferentially deposited, since its percentage in the deposit is always higher than its metal percentage in the bath; and thus it may in some way hinder nickel from assuming its normal deposition potential. Consequently, the data depict that under the present conditions the electrodeposition of cobalt–nickel alloys belongs to the anomalous-type [12]. However, numerous studies were carried out to explain this phenomenon [13–16].

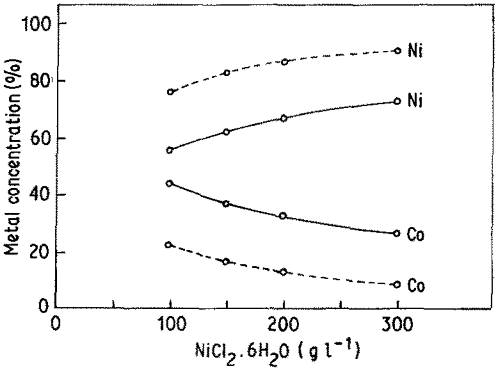

Fig. 8. The percentages of cobalt and nickel in the alloys deposited from baths (Co–Ni) 5, 6, 3 and 7 (solid lines). The broken lines represent the metal percentages in the alloy baths. Plating time was 15 min at a current density of 7 A dm^{-2}.

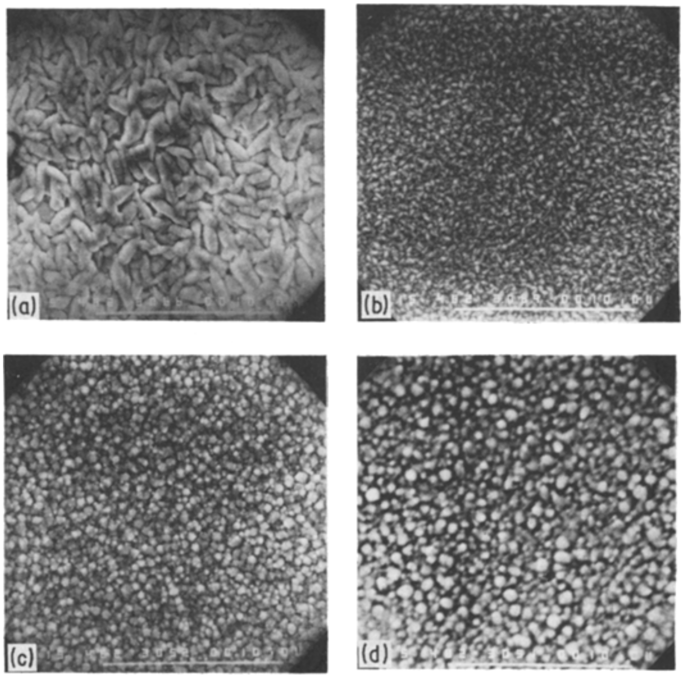

Fig. 9. Electron micrographs of (a) cobalt from bath Co. 3, (b) nickel from bath Ni. 3, (c) and (d) cobalt–nickel alloys from baths (Co–Ni) 3 and 8, respectively (magnifications at 3880 ×).

Fig. 7 shows that as the Co% in the bath increases slightly, there is a considerable increase of the Co% in the alloy. This is a reasonable result and could be correlated to the fact that the cathode diffusion layer becomes relatively more depleted with respect to the preferentially depositable Co^{2+} ions. Therefore, increasing the Co% in the bath tends to oppose the depletion of the Co^{2+} ion in the cathode layer and accordingly increases the Co% in the electrodeposited alloy. On the other hand, Fig. 8 establishes that the Ni% in the alloy increases in a parallel manner to increasing the Ni% in the bath. This indicates that the test system seems to be in equilibrium with respect to Ni^{2+} ions which are present in a high concentration.

3.4. *Surface morphology*

The structures of cobalt, nickel and cobalt–nickel alloys deposited from the present baths at a current density of 1 A dm^{-2} and duration of 10 min, were examined by a scanning electron microscope. Some of the electron micrographs taken are shown in Fig. 9 at a magnification of 3880 ×.

The cobalt deposit from the sulphate bath Co. 3 consists of elongated dihedral grains leaving no holes between them and oriented at random (Fig. 9a). A similar structure was observed for cobalt deposits from a chloride bath [17]. The nickel deposit from the chloride bath Ni. 3 shows a finer-grained texture and an increased nucleation density (Fig. 9b). Fig. 9c shows that the cobalt–nickel alloy from Watts bath (Co–Ni) 3 consists of nodular grains having an intermediate size between those of the parent cobalt and nickel deposits from the corresponding individual baths. Inspection of Figs. 9a, b depicts that although the overpotential of cobalt deposition (see Fig. 1) is greater than that of nickel (see Fig. 2) the grain size of the cobalt deposit is larger. This could be referred partly to the specific properties of the metals and partly to the difference in adsorbabilities of the SO_4^{2-} and Cl^- anions on the surface of the copper cathode [18]. This suggestion was confirmed by replacing $NiCl_2$ in bath (Co–Ni) 3 by $NiSO_4$, containing an equal Ni content, in bath (Co–Ni) 8 where a coarser grained alloy deposit was obtained (Fig. 9d). It is worth noting that chemical analysis revealed that cobalt–nickel alloys from baths (Co–Ni) 3 and 8 have almost the same composition and contain 59.2% and 60% cobalt, respectively. In addition, our results agree

Table 2. Characteristics of X-ray diffraction patterns of cobalt–nickel alloys. Sample I deposited from bath (Co–Ni) 1 and contains 93.7% nickel. Sample II deposited from bath (Co–Ni) 4 and contains 45.1% nickel

Sample	d *(Å)*	I/I_0	*Phase (f c c)*	*h k l*	a *(Å)*	*Average value of* a *(Å)*	
						α(Co)	*β(Ni)*
I	2.042	100.00	α(Co)	1 1 1	3.536	3.529	3.625
	1.812	53.71	β(Ni)	2 0 0	3.624		
	1.764	22.86	α(Co)	2 0 0	3.528		
	1.282	42.85	β(Ni)	2 2 0	3.626		
	1.246	21.14	α(Co)	2 2 0	3.524		
II	2.050	100.00	α(Co)	1 1 1	3.550	3.530	3.623
	1.812	70.00	β(Ni)	2 0 0	3.624		
	1.751	28.42	α(Co)	2 0 0	3.502		
	1.282	34.21	β(Ni)	2 2 0	3.626		
	1.251	15.79	α(Co)	2 2 0	3.538		
	1.091	38.95	β(Ni)	3 1 1	3.618		

with those of Young and Struyk [15] who reported that the cobalt–nickel deposit from an all-chloride bath was finer-grained than the one from a corresponding all-sulphate bath.

Cobalt–nickel alloys deposited from the present Watts baths have a white colour and are sound, smooth and bright. The smoothness and brightness of the deposits increase with an increasing nickel content in the bath.

3.5. *X-ray diffractometry*

X-ray diffraction analysis was carried out on the cobalt–nickel alloys prepared from the Watts bath under test, at a current density of 5.3 A dm^{-2} and duration of 10 min, and some examples of the results are given in Table 2.

The data indicate that, irrespective of the bath or alloy composition, the cobalt–nickel alloys are deposited in the face-centred cubic structure and consist of a mixture of α(Co) and β(Ni) phases. Moreover, it is observed that the lattice parameter a of nickel increases from 3.52 Å as a result of the formation of the alloy in the β(Ni)-phase. On the other hand, the lattice parameter of cobalt (3.54 Å) was not affected by the formation of the α(Co)-phase alloy which almost has the same lattice parameter (3.53 Å). These results are in good agreement with those reported earlier in literature [19–21].

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