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Effects of cobalt, temperature and certain impurities upon cobalt electrowinning from sulfate solutions

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Abstract

The effects of cobalt concentration, temperature and the presence of zinc, copper and iron ions in the electrolyte on current efficiency and cathodic quality were investigated by cyclic voltammetry and galvanostatic methods during cobalt electrowinning. The results showed that high cathodic efficiency of cobalt deposition was obtained from solutions containing cobalt concentration in the range 30–60 g l^{-1}. Current efficiency increased from 94% to 97% with increase in cobalt concentration to 60 g l^{-1} at 20 °C. It was also found that increase in temperature to 50 °C enhanced the cobalt deposition reaction, along with the rate of hydrogen evolution, resulting in little change in current efficiency. The presence of foreign cations in the electrolyte not only adversely affects current efficiency but also promotes cracking and peeling.

1. Introduction

Cobalt is a very important metal because of its many industrial and strategic uses related to its high melting point, its allotropic nature and ferromagnetic properties [1]. Cobalt is usually extracted in small quantities as a byproduct from nonferrous metals production. It is associated with zinc and precious metals recovery. Cobalt is recovered mainly by hydrometallurgical processes in which the final step of recovery is generally electrowinning [1, 2]. A brief summary of the theoretical background concerning cobalt electrowinning has been given [3]. To date, the most popular electrowinning recovery process for cobalt metal involves a sulphate medium [2–7]. Most of the baths contain boric acid to buffer the pH of the solution and the cathodic film. Boric acid generally acts as a brightening agent, as well as a cathode polarizer for the electrodeposition of cobalt [6].

To obtain optimum energy consumption and product quality, the electrolyte must be free from any significant concentrations of impurity elements. The major impurity elements of concern include Zn, Cu, Fe, Mn, Mg, Cd and Se [1]. The presence of metal ion impurities is known to affect the electrodeposition of cobalt [4, 6, 8]. Extensive electrolyte purification is essential to decrease the concentration of the harmful impurities to acceptable levels.

Jeffrey et al. [4] found that zinc affects cobalt deposition, but only when it is present in high concentration (>100 ppm). Zinc was reported to decrease the current efficiency by inhibiting electrocrystallization [9, 10]. Iron in cobalt electrolytes has been described as a harmful impurity because it decreases the cathodic current efficiency [4].

Today, most of the world's cobalt is produced by electrowinning; despite this, there is currently very little fundamental knowledge about the behaviour of impurities on the electrowinning process. Their effects on cathode cobalt thus required investigation.

2. Experimental details

2.1. *Electrolyte preparation*

A stock solution of cobalt sulphate, 60 g l^{-1} Co, and 30 g l^{-1} free boric acid was prepared by using pure reagents and distilled water. Electrolytes with various cobalt concentrations were prepared by mixing appropriate volumes from the concentrated solution and 30 g l^{-1} boric acid solution. The bulk pH was adjusted to a value of 4 using sodium hydroxide or sulfuric acid. The various trace impurities of zinc, copper and iron cations were introduced into the electrolyte as sulfate. All the chemicals used were of analytical grade.

2.2. *Cyclic voltammetry*

A conventional three-electrode configuration was employed. The working electrode was a rotating glassy carbon electrode, GCE, 4 mm diameter purchased from

EG&G Instruments. The reference electrode was a saturated mercurous sulfate electrode, MSE, $E=$ 650 mV vs standard hydrogen electrode (SHE). The auxiliary electrode was a graphite rod with an exposed surface area of greater than 10 cm^2. The voltammetric response was obtained from a Potentioscan Pos 73, (Wenking), coupled to a personal computer to record current and voltage. Polarization curves were generated by sweeping cathodically from 150 to −1450 mV vs MSE at different scan rates. All potentials are given against the above reference electrode.

2.3. *Galvanostatic deposition*

Cobalt electrodeposition experiments were carried out using an electrolytic cell, provided with a reservoir and a circulating pump. The electrolysis cell consisted of a Pyrex 600 ml jacketed beaker fitted with a Perspex cover with slots to mount the electrodes. Copper sheets of 5 cm^2, 0.3 mm thicknesses, encased in a Perspex holder, were used as cathodes. A platinum sheet measuring 3 cm × 6 cm was used as the anode. It was sheathed in a polypropylene cloth bag. A peristaltic pump, (Cole–Parmer Instrument Company, MasterFlex L/S, model 7518-00), was used for maintaining the flow rate of the electrolyte at 2 ml min^{-1}. The total volume of the electrolyte amounted to 1 L. This relatively large electrolyte volume used ensured a minimum change in concentration during the electrowinning test. The electrolysis was carried out by applying constant current from a regulated power supply (0–25 V, 8 A, d.c. power supply, IMPO type rectifier, model FBS 1101).

In this series of experiments, the quantity of electricity was kept constant at 900 C while using different current densities for different periods. At the end of the electrolysis, the cathode holder was quickly removed from the solution. The cathode was thoroughly washed with tap water followed by distilled water and ethanol, and dried and accurately weighed. The current efficiency was calculated from the cathode weight gain and the number of coulombs passed.

3. Results and discussion

3.1. *Cyclic voltammetry*

The deposition of cobalt was initially studied using cyclic voltammetry. The influence of electrolysis parameters on one-cycle polarization tests is observed in Figures 1–6.

A representative plot of the cyclic voltammograms, CVs, for the GCE in 60 g l^{-1} cobalt solutions at 20 mV s^{-1} and 100 mV s^{-1} is given in Figure 1. During the scan in the negative direction, the current increases sharply once cobalt nucleation begins. These curves indicate that cobalt reduction on the GCE starts at −1030 mV and −1080 mV at 20 mV s^{-1} and 100 mV s^{-1}, respectively. Due to hydrogen evolution, an increase in the current density is observed at more cathodic potential and no clear limiting current density is observed.

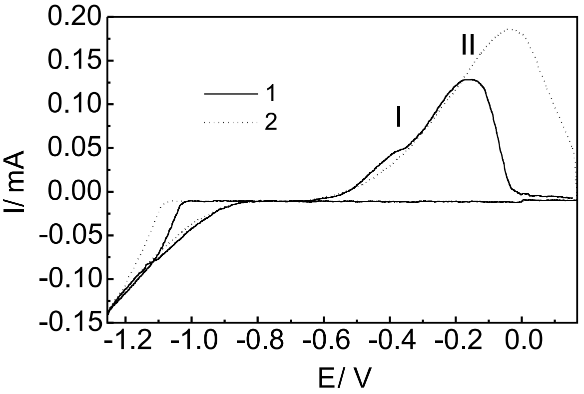

Fig. 1. Cyclic voltammograms for cobalt deposition and stripping on GCE in 60 g l^{-1} Co + 30 g l^{-1} boric acid at (1) 20 and (2) 100 mV s^{-1}. Temp. 20 °C.

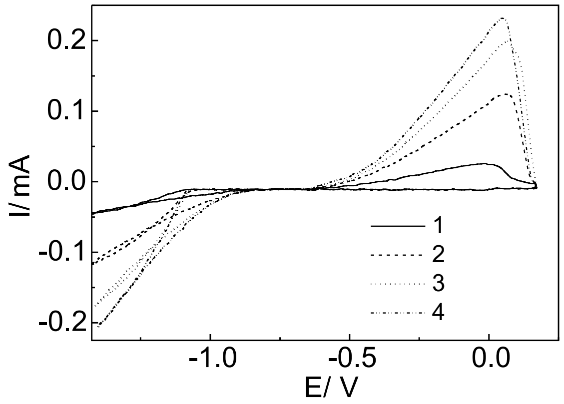

Fig. 2. Cyclic voltammograms for cobalt deposition and stripping on GCE in various cobalt concentrations + 30 g l^{-1} boric acid, pH 4 solutions at 20 °C 20 mV s^{-1}. Cobalt conc.: (1) 5, (2) 20, (3) 40 and (4) 60 g l^{-1}.

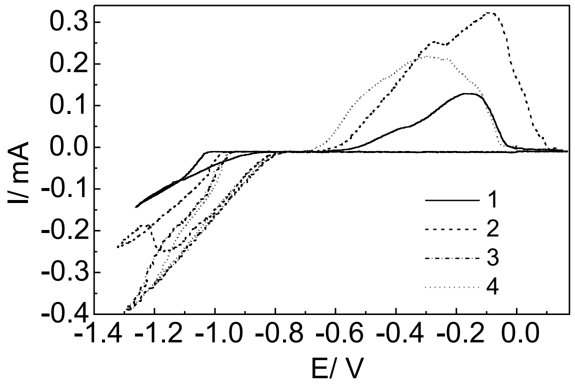

Fig. 3. Cyclic voltammograms for cobalt deposition and stripping on GCE in 60 g l^{-1} Co + 30 g l^{-1} boric acid, 20 mV s^{-1} at various temperatures; (1) 20, (2) 40, (3) 50 and (4) 60 °C.

It is assumed that both cobalt and hydrogen are plated cathodically first and then only cobalt is dissolved

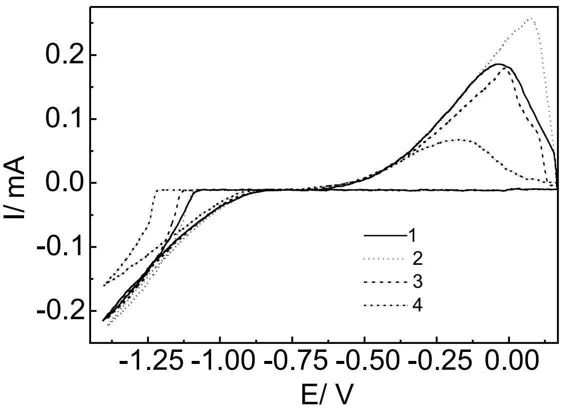

Fig. 4. Cyclic voltammograms for cobalt deposition and stripping on GCE in 60 g l^{-1} Co + 30 g l^{-1} boric acid, in presence of various zinc concentrations: (1) 0, (2) 300, (3) 500 and (4) 800 ppm at 100 mV s^{-1}, 20 °C.

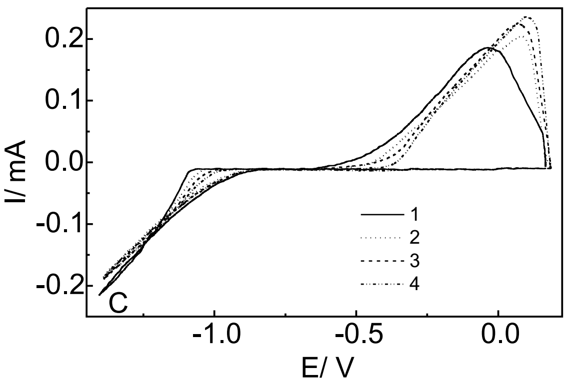

Fig. 5. Cyclic voltammograms for cobalt deposition and stripping on GCE in 60 g l^{-1} Co + 30 g l^{-1} boric acid, in presence of various copper concentrations: (1) 0, (2) 50, (3) 300 and (4) 800 ppm at 100 mV s^{-1}, 20 °C.

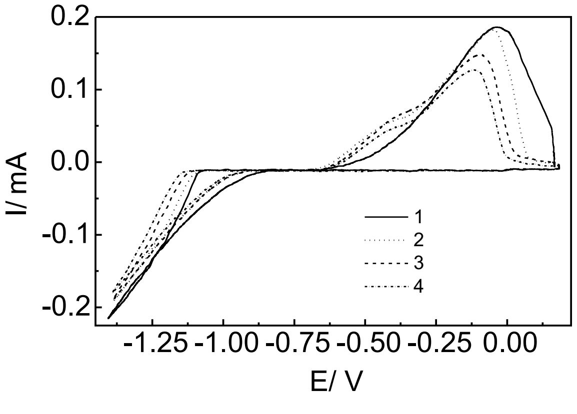

Fig. 6. Cyclic voltammograms for cobalt deposition and stripping on GCE in 60 g l^{-1} Co + 30 g l^{-1} boric acid, in presence of various iron concentrations: (1) 0, (2) 100, (3) 250 and (4) 400 ppm at 100 mV s^{-1}, 20 °C.

anodically. Upon reversing the scan direction, the current decreases and reaches zero. Then the current becomes anodic corresponding to the dissolution of the deposited cobalt. During the reversing sweep at a scan rate 20 mV s^{-1}, two anodic peaks I and II are observed whereas one anodic peak occurs in the case of 100 mV s^{-1}. Nosang Myung et al. [5] reported that the two anodic peaks are associated with the dissolution of cobalt from the GCE surface to the solution from two different cobalt metal phases. Similar multiple peaks were also observed by Jaya et al. [11].

The main cathodic reactions occurring in cobalt electrowinning are:

$$\mathrm{Co}^{2+} + 2\mathrm{e}^- = \mathrm{Co} \quad E^\circ = -0.227\,\mathrm{V} \tag{1}$$

$$2\mathrm{H}^+ + 2\mathrm{e}^- = \mathrm{H}_2 \quad E^\circ = 0\,\mathrm{V} \tag{2}$$

The production of hydrogen gas occurs because cobalt is less noble than the hydrogen electrode, as can be seen from the standard reduction potential of cobalt. The hydrogen evolution reaction is obviously not desirable because it represents a loss of useful current, and, therefore, it must be kept to a minimum by maintaining the pH at 4.

3.1.1. *Effect of cobalt concentration*

The effect of cobalt concentration, in the range 5 to 60 g l^{-1}, on the CVs is shown in Figure 2. Voltammograms of cobalt reduction show that increasing the cobalt concentration causes a gradual increase in cathodic current. The initial deposition overpotential does not show an appreciable change; the curves do depolarize more as the scan proceeds toward more cathodic potential. It can be seen that, as the cobalt concentration increases, the current density shifts to more positive potentials denoting an increase in electrocrystallization. This decrease in potential relates to a significant saving in energy consumption when electrowinning from more concentrated cobalt solutions is performed. This aspect is in accordance with previously reported results [2, 4].

The CVs show that as the cobalt concentration is increased, the area covered by the anodic curve is increased, that is, the charge related to anodic stripping is increased. This can be connected with the increase in cobalt deposition efficiency during the cathodic process with increase in solution cobalt concentration.

3.1.2. *Effect of electrolyte temperature*

Figure 3 shows the effect of temperature on cobalt polarization for deposition–dissolution reactions from 60 g l^{-1} cobalt solution at 20 mV s^{-1}. The cathodic polarization declines with temperature. A depolarizing effect is demonstrated with increase in temperature and the curves depolarize more with increasing potential. When electrodeposition was carried out at 20, 40, 50 and 60 °C, the cobalt nucleation overpotential decreased by 45, 75 and 80 mV, respectively. The increase in temperature from 20 to 50 °C results in a significant decrease in cathodic polarization.

Upon reversing the scan direction, Figure 3 shows that as the temperature of the electrolyte is increased, the slope of the anodic branch is steeper and cobalt dissolution is less polarized. This means that the increase in temperature also activates cobalt dissolution. The anodic current peak increases with increase in temperature up to 50 °C. The anodic peaks at 40 °C and 50 °C (curves 2 and 3) are superimposed. Beyond this temperature the current peak starts to decrease. Redissolution (curve 4) at 60 °C is less than at 50 °C (curve 3).

Clearly these data show that temperature has an effect on the cobalt deposition and dissolution reaction. Increasing the electrolyte temperature appears to enhance the deposition reaction. However, it was found that the hydrogen evolution reaction occurs more readily at higher temperature. To determine if this effect outweighs the gain in the cobalt deposition reaction, the current efficiency was calculated at different temperatures as seen later. The increase in temperature was found to affect cathodic cobalt deposition more than the cobalt concentration of the electrolyte.

3.1.3. *Effect of impurities*

Cobalt deposition was studied in the presence of common plant impurities, including zinc, copper and iron.

(a) *Effects of zinc*. The deposition of cobalt from 60 g l^{-1} cobalt solution in the presence of 0–800 ppm zinc, at 20 °C and 100 mV s^{-1}, was studied. Figure 4 shows that the anodic current peak increases gradually with increase in zinc concentration up to 300 ppm. Upon further addition in zinc to 500 ppm, there is a slight decrease in the anodic current peak compared to that obtained with zinc-free solution. When the zinc concentration is further increased to 800 ppm, the anodic current peak decreases sharply.

Zinc has a more negative potential than cobalt. The standard potentials of cobalt and zinc differ by 0.5 V, (i.e., −0.277 and 0.76 V, respectively). Thus cobalt will deposit preferentially. Under the influence of the electric field, zinc cations migrate toward the electrode, build up near the cathode surface and hinder the approach of cobalt ions. The inhibition of cobalt reduction by zinc is related to another well-known phenomenon: the anomalous codeposition of zinc–cobalt alloys [12]. Dahms and Croll [13] suggest that the insoluble hydroxide of the less noble metal formed near the electrode, due to local pH increase, inhibits further reduction of the more noble metal. Pas and Dreisinger [14], who have argued that the pH in the vicinity of the electrode may not be high enough to precipitate insoluble zinc hydroxide, attribute the inhibition of cobalt reduction to the underpotential deposition of a zinc layer. The inhibition of cobalt electroreduction, however, has also been observed even when a very small amount of zinc is present [15].

(b) *Effects of copper*. Typical cyclic voltammograms are shown in Figure 5. The anodic current peak increases with the addition of copper. In all copper concentrations, the corresponding anodic peak potential shifts positively. The anodic dissolution of cobalt starts at less negative potential values with increase in copper concentration. An increase in anodic area indicates that the cathodic current efficiency increases with increasing copper concentration.

(c) *Effects of iron*. The CV curves are given in Figure 6. The anodic current of cobalt dissolution starts at less positive potential and the anodic current peak decreases with increase in iron ions in solution. The two anodic peaks, I and II, are well developed as the iron concentration increases. Their potentials become more cathodic with increase in electrolyte iron content. A gradual decrease in anodic current peak indicates that the current efficiency in the cathodic process decreases with increase in iron concentration.

Iron cations change the deposition mechanism, and inhibit the early stages of cobalt nucleation and growth [9]. Iron has also been reported to result in anomalous cobalt deposition, due to hydrogen evolution in the vicinity of the cathode [15, 16].

The presence of zinc, copper and iron cations in solution changed the CV profiles, which suggests that changes in the electrochemical reactions do occur. However, the current efficiency and deposition morphology are not easily or readily interpretable from these curves.

3.2. *Current efficiency and energy consumption*

The cathodic depositions of cobalt from both 60 and 30 g l^{-1} Co^{2+} solutions were carried out galvanostatically at different current densities and temperatures. The effect of current density during cobalt electrowinning on cell voltage, cathode potential, current efficiency (CE) and energy consumption (EC) was followed.

The results indicated that both the cell voltage and cathode potential during cobalt electrowinning increased with increase in current density and decreased with increase in cobalt concentration and electrolyte temperature. This decrease was sharp at 50 °C. The power consumption was found to increase with increase in current density which is mainly due to variations in the cell voltage and current efficiency.

Two sets of results with 30 and 60 g l^{-1} Co solutions at 20 and 50 °C, given in Table 1, show somewhat different

Table 1. Results of cobalt electrowinning from cobalt sulfate and 30 g l^{-1} boric acid solutions, pH 4, at 20 and 50 °C

	Co /g l^{-1}	CD /mA cm^{-2}	CE /%	EC /kWh kg^{-1} Co
50 °C				
1	30	10	90	2.49
2	30	50	94	4.33
3	60	10	94	1.92
4	60	50	97	3.28
20 °C				
5	30	10	–	–
6	30	50	94.3	3.84
7	60	10	–	–
8	60	50	99	2.85

behaviour. Increasing the cobalt concentration to 60 g l^{-1} appeared to increase the current efficiency compared to deposition tests using 30 g l^{-1} Co^{2+} electrolyte.

Increasing the current density from 10 to 50 mA cm^{-2} increases the current efficiency by about 4%, while the increase in electrolyte temperature to 50 °C slightly improves the current efficiency. Cobalt electrowinning from 50 °C electrolyte containing 60 g l^{-1} cobalt at lower current density, 10 mA cm^{-2}, produced deposits of poor morphology and accurate current efficiency values could not be obtained. Cobalt electrowinning at 50 mA cm^{-2} achieved 99% efficiency.

One advantage of operating at higher temperature is that a lower potential is required. There is a small gain in specific energy consumption which decreases to 2.85 kWh kg^{-1} Co with 60 g l^{-1} Co solutions at 50 mA cm^{-2}. The efficiency of cobalt deposition from 60 g l^{-1} cobalt solutions at 20 °C in the presence of different foreign ions was examined at 10 and 50 mA cm^{-2}. The results in Table 2 reveal that the presence of foreign cations leads to lower current efficiency and higher energy consumption.

Up to 100 ppm zinc has a limited effect on the cobalt deposition efficiency at higher current density (50 mA cm^{-2}). The effect of the presence of zinc cations is more detectable with increase in their concentration. With 300 ppm Zn the current efficiency was not measurable at 10 mA cm^{-2}, due to the degraded morphology where the deposits were extensively cracked and curled. At 50 mA cm^{-2}, the deposits were more coherent and the current efficiency was 93% which is lower than the results for zinc-free cobalt solutions.

Copper had a strong effect on the cobalt deposition efficiency. The cathodic current efficiency fell rapidly at 10 mA cm^{-2} to 70% and 58% in presence of 50 and 300 ppm copper, respectively.

The influence of the presence of iron in solution was also studied. Electrowinning of cobalt at 10 mA cm^{-2} gives 71% and 67% current efficiencies in the presence of 100 and 300 ppm iron, respectively. At 50 mA cm^{-2}, an efficiency value of about 90% was achieved.

The results show that the current efficiencies fell drastically at lower current density, 10 mA cm^{-2}, with all the tested foreign cations. Generally, the current efficiency was significantly lower than for prior deposition tests using pure cobalt electrolyte. On the other hand, it was observed that the presence of 100 ppm Zn combined with either 100 ppm Cu and/or 100 ppm Fe in solutions gives an efficiency of less than 94% at 50 mA cm^{-2}.

3.3. *Morphology*

The various deposit morphologies obtained from electrolysing both cobalt solution and solutions containing zinc, copper and iron ions separately or in admixture were examined.

The temperature of the electrolyte has a marked effect on the deposit. Poor morphology and brittle deposits were obtained at 50 °C, especially at lower current density. Electrodeposition of cobalt from 60 g l^{-1} cobalt solutions at 10 mA cm^{-2} and 50 °C resulted in poor, brittle and degraded deposits. The copper substrate coverage is very poor and the deposits detach from the substrate. At 50 mA cm^{-2}, flat deposits are obtained (Figure 7). The deposit consists of patches of grainy type growth with individual crystals without clear texture.

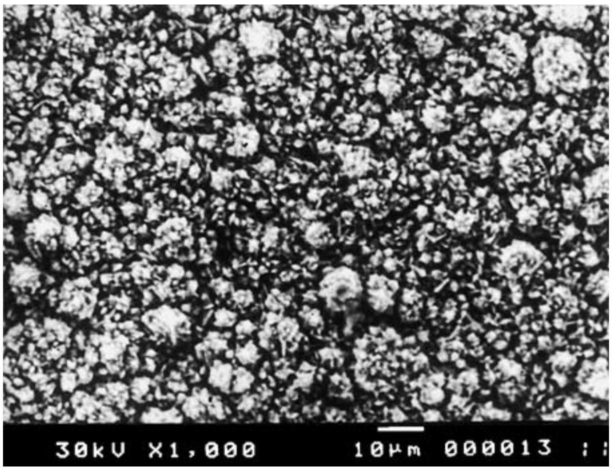

Fig. 7. Scanning electron micrograph of cobalt electrowon from 60 g l^{-1} Co and 30 g l^{-1} boric acid solution, at 50 mA cm^{-2}, 50 °C.

Table 2. Results of cobalt electrowinning from 60 g l^{-1} cobalt and 30 g l^{-1} boric acid solutions, pH 4, in presence of foreign cations, at 20 °C

No.	Zinc /ppm	Copper /ppm	Iron /ppm	CD /mA cm^{-2}	CE /%	EC /kWh kg^{-1} Co
1	100	–	–	10	87	3.35
2	100	–	–	50	97	3.68
3	300	–	–	10	–	–
4	300	–	–	50	94.3	3.5
5	–	50	–	10	70	3.13
6	–	50	–	50	94.8	3.88
7	–	300	–	10	58	3.68
8	–	300	–	50	91	3.65
9	–	–	100	10	71	3.1
10	–	–	100	50	91	3.88
11	–	–	300	10	67	3.18
12	–	–	300	50	90	3.57

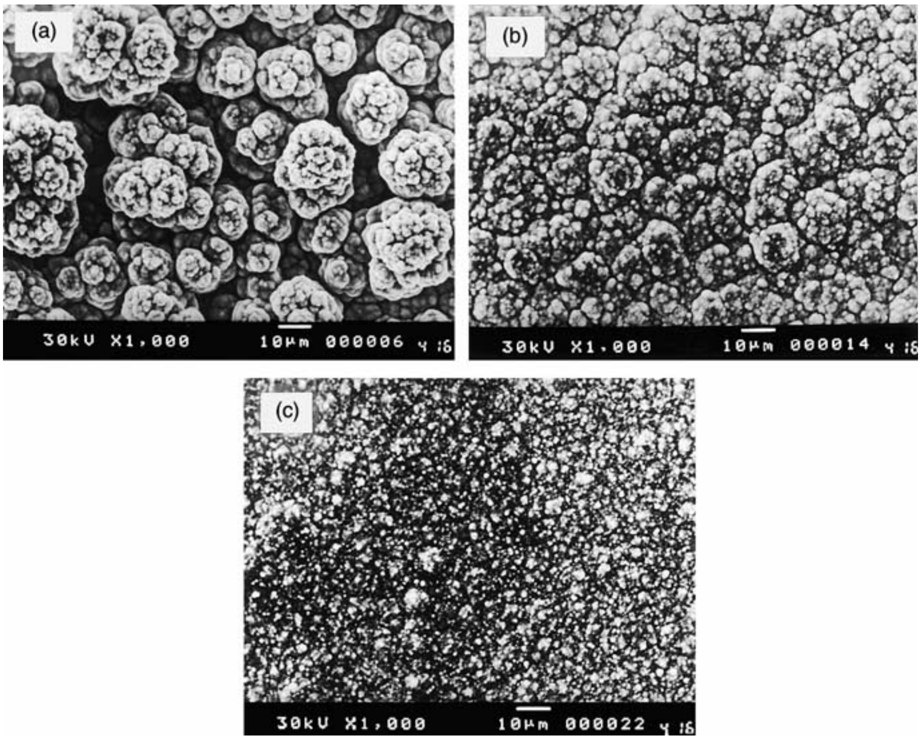

Fig. 8. Scanning electron micrograph of cobalt electrowon from 60 g l^{-1} Co and 30 g l^{-1} boric acid solution in presence of (a) 300 ppm Zn, (b) 300 ppm Cu, and (c) 300 ppm Fe, at 50 mA cm^{-2}, 20 °C.

Another series of deposition tests from 60 g l^{-1} cobalt solutions was conducted at 20 °C to investigate the effects of zinc, copper and iron.

The deposit obtained in presence of zinc in solution gave a coarse and relatively rough structure. With higher zinc concentration (300 ppm), the deposit was rough and blackish grey at 50 mA cm^{-2}. Figure 8(a) shows that a nodular deposit with cauliflower-like dendrites is obtained. Higher concentration of Cu, 300 ppm, produced flat, dark grey deposits. At 50 mA cm^{-2} the shape and size of the crystals decreased (Figure 8(b)), with a reasonably smooth and dense deposit. The addition of 300 ppm Fe produced spherically shaped crystals with a finer structure at 50 mA cm^{-2} (Figure 8(c)).

The effects of the presence of zinc in conjunction with copper and/or iron was investigated. Here grainy and dark grey deposits were obtained. In the presence of Zn, Cu and Fe admixture cations, the deposit was nodular, consisting of polyhedral crystals of varying sizes as shown in Figure 9. This deposit was curled and easily peeled off.

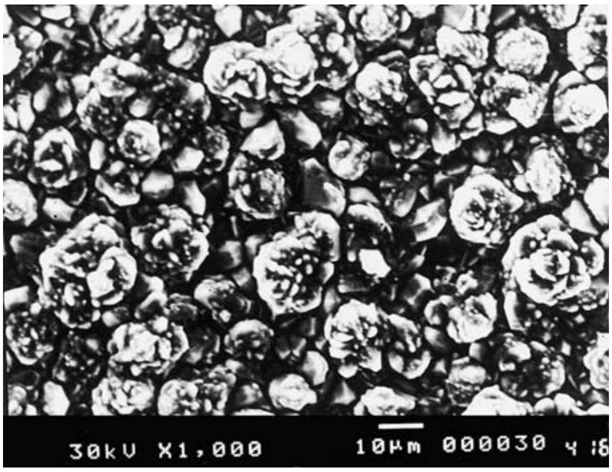

Fig. 9. Scanning electron micrograph of cobalt electrowon from 60 g l^{-1} Co and 30 g l^{-1} boric acid solution in presence of 100 ppm Zn + 100 ppm Cu + 100 ppm Fe, at 50 mA cm^{-2}, 20 °C.

4. Conclusions

Cobalt electrowinning experiments from sulphate solutions were carried out. Increasing cobalt concentration from 30 to 60 g l^{-1} in 20 °C electrolyte, caused the current efficiency to increase by about 3%, reaching 98% at 50 mA cm^{-2}. It can be concluded that the effect of temperature on the current efficiency is moderate. However, an adverse effect of higher temperature is poor morphology.

The presence of zinc and iron cations in the electrolyte produces a polarizing effect. On the other hand, copper cations have a depolarizing effect. The impurities exert a deleterious effect upon current efficiency as well as upon the morphology and purity of the deposits.

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