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RECOVERY OF COPPER AND COBALT FROM LOW COPPER Cu-Co-Fe ALLOY

ODZYSK MIEDZI I KOBALTU Z NISKOMIEDZIOWEGO STOPU Cu-Co-Fe

Recovery of copper and cobalt from the electrolyte and the slime produced during anodic dissolution of Cu5Co25Fe70 alloy in ammonia-ammonium chloride solution was carried out. Anodic dissolution resulted in a separation of metals, with iron remaining mainly in the slime and cobalt deposited on the cathode or left in the slime, while most copper accumulated in the slime. A part of copper and cobalt still remained in the electrolyte. The chemical composition of the slime was determined. The slime was a mixture of $CoO \cdot Fe_2O_3 + Fe_2O_3 \cdot H_2O$ with some CuO addition. This slime was dissolved in a sulphuric acid. The removal of iron from the solution before the electrowinning was required, in spite of high losses of valuable metals during iron hydroxide precipitation. Regulation of pH enables the selective electrowinning of copper and cobalt from solutions. The cathodic deposits of high purity were obtained, however the cathodic efficiencies were not too high. The total recovery of copper and cobalt from the alloy was 66% and 56%, respectively. The residual amounts of copper and cobalt remained mainly in the iron precipitates.

Keywords: cobalt, copper, electrowinning, slime

Przeprowadzono odzysk miedzi i kobaltu z elektrolitu i szlamu otrzymanych w procesie anodowego roztwarzania stopu Cu5Co25Fe70 w roztworze amoniakalno-chlorkowym. Anodowe roztwarzanie umożliwia rozdział metali: związki żelaza stanowią główny składnik szlamu, kobalt wydziela się na katodzie lub pozostaje w szlamie, miedź gromadzi się głównie w szlamie. Część kobaltu i miedzi pozostaje w elektrolicie. Określono skład chemiczny szlamu - stanowił on mieszaninę $CoO \cdot Fe_2O_3 + Fe_2O_3 \cdot H_2O$ i CuO. Szlam roztworzono w kwasie siarkowym. Odzysk miedzi i kobaltu z roztworu wymaga usunięcia jonów żelaza z roztworu za pomocą stężonego roztworu amoniaku, pomimo iż prowadzi to do znacznych strat cennych metali. Odpowiedni dobór pH roztworu umożliwia selektywny odzysk miedzi i kobaltu z roztworów. Uzyskano osady katodowe o wysokiej czystości przy stosunkowo niskich katodowych wydajnościach prądowych. Całkowity odzysk miedzi i kobaltu ze stopu wynosi, odpowiednio: 66% i 56%.

1. Introduction

A recovery of nonferrous metals (eg. copper, cobalt, nickel) from scraps and metallurgical slags has been practiced for many years. Qualitative and quantitative compositions of industrial wastes impose conditions on its treating. Typical scheme for hydrometallurgical processing is: leaching or anodic dissolution, and then selective separation of metals from solution either in the metallic form or as salts. Sulphuric acid is most often used as dissolving reagent, however ammoniacal solutions seem to be an attractive alternative. The main feature of ammonia solutions is leaving substantially all iron in a residue, while other metals are transferred into solution as soluble ammine complexes.

This work is a part of a series of investigations carried out on metal recovery from synthetic Cu-Co-Fe alloys [1, 2]. It was found that dissolution of the Cu-Co-Fe alloys in ammoniacal solutions [1, 3] was strictly determined by their phase composition. The high-copper alloy (90%Cu) dissolved spontaneously in Cu^{2+}-ammonia-ammonium sulphate solution (in contact with the air) resulting solely in copper accumulation in the leaching solution, while cobalt and iron remained in the solid phase (as a slime). Recovery of copper from that solution [4] and cobalt from the slime [5] was carried out. Low-copper alloys (5%Cu) were unaffected by chemical leaching, but did dissolve during electrolysis in ammonia-ammonium chloride solution [1]. The anodic dissolution resulted in a separation of metals with iron

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remaining mainly in the slimes, and cobalt as a main component of the cathodic deposits and of the slimes. Copper accumulated mainly in the slimes. The aim of this study was to conduct hydrometallurgical treatment of the ammoniacal solution and the slime generated during anodic dissolution of Cu5Co25Fe70 alloy in order to recover both: copper and cobalt.

2. Experimental

The scheme of the alloy treatment is shown in Fig. 1. At every stage of the processing, the volume and composition of the solutions were controlled. Concentrations of copper, cobalt and iron ions in all solutions were determined using AAS method (Perkin Elmer Atomic Absorption Spectrometer 3110).
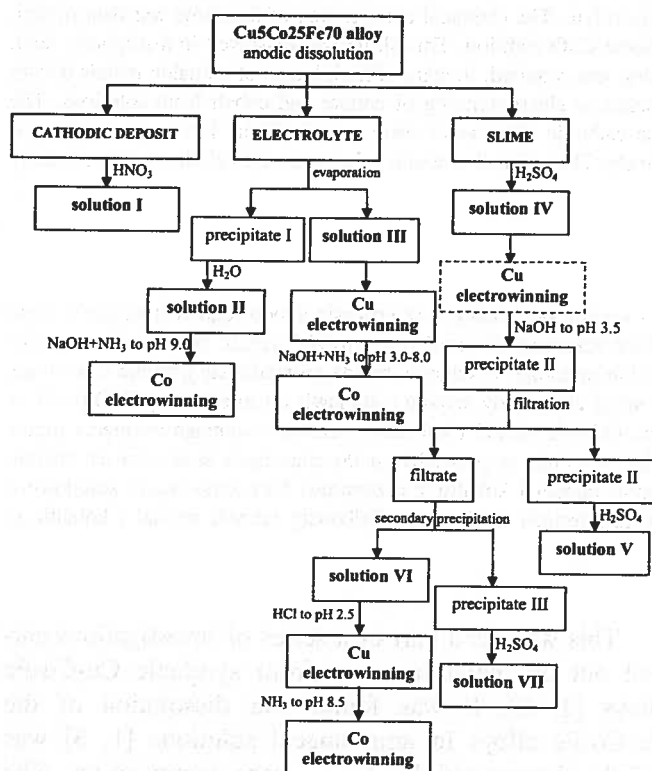

Fig. 1. Schematic chart of the Cu5Co25Fe70 alloy processing

2.1. Anodic dissolution of Cu5Co25Fe70 alloy

A block sample of synthetic alloy was placed between two platinum cathodes in a cuboid PVC vessel containing 1 dm^3 of electrolyte. The solution contained the mixture of 2.5 M (NH$_3$ + NH$_4^+$) and 0.5 M Cl$^-$. The pH of the solution was 10. The bath temperature was maintained at 50±0.1 °C. The electrolyte was agitated with the magnetic stirrer. The copper coulometer was

connected to the electric circuit. The anodic dissolution was conducted at constant current intensity of 0.88 A, which corresponded to the initial anodic current density of 350 A/m^2 (initial anode area was 25.1 cm^2). Every 5 h the solution was filtered and replaced with the fresh ammoniacal electrolyte. In the same interval the anode was taken out of the solution and the slime was mechanically removed from the specimen surface. These operations were repeated (in 9 stages) until about 40 g of alloy (41,591 g) dissolved in the electrolyte. Each slime portion (from filtered electrolyte and the anode) was washed with distilled water, dried at 55 °C (to evaporate the water) to obtain the stable mass of the sample and collected. All electrolytes and slime washings were accumulated. The cathodic deposits were removed from the substrates after 45 h of electrolysis (after last stage). Both deposits were dissolved in 0.2 dm^3 7 M HNO$_3$ (solution I). The electrolysis parameters and duration of each stage followed from our earlier work [1], which showed inhibition of the anode dissolution after 6 h of the process as a result of the slime accumulation on the anode surface. However, it was found that periodical removing of the slime enables further anode dissolution.

2.2. Processing of the electrolyte

Over 15 dm^3 of the final electrolyte was obtained after the anodic dissolution processes. Next, it was reduced to the volume of about 2 dm^3 by evaporation, and consequently a precipitation from the solution occurred. The addition of a few cm^3 of concentrated H$_2$SO$_4$ to this solution did not dissolve precipitated compound (precipitate I). Therefore, it was filtered and then dissolved in 0.5 dm^3 H$_2$O. Obtained solution (solution II) contained mainly cobalt ions and after pH adjustment from 2.1 to 9, cobalt electrowinning was carried out.

The filtrate was filled with water up to the volume of 2 dm^3 (solution III). The pH of this solution was 0. From 1 dm^3 of the solution III copper electrowinning was carried out. After the complete copper recovery, the solution was alkalized with sodium hydroxide and concentrated ammonia, and a series of electrolysis's at various pH was conducted in order to recover cobalt left in the solution.

All electrolysis's were conducted in a cuboid PVC vessel at room temperature. Rectangular platinum cathode was suspended between two platinum anodes. The electrolyte was agitated with the magnetic stirrer with rotation rate of 900 rpm. The copper coulometer was connected in the electric circuit. The process was conducted at constant cathodic current density. Its value was gradually decreased in consecutive stages to prevent metallic powder electrodeposition as the concentration of metal ions in the bath decreased with time. Details of all

TABLE 1

Parameters of copper and cobalt electrowinning

Electrowinning	Time. h		Current density. A/m²	pH	Electrolyte volume. dm³
	stage	total			
solution II					
cobalt	4	4	25		0.5
	10	14	10	9.0	0.495
	5	19	10		0.490
solution III					
copper	3	3	40		1
	3	6	20		0.995
	5	11	10	0	0.990
	2	13	10		0.985
	3	16	10		0.980
	1	1		3.0	1.14
	1	2		5.5	1.14
	10	12		5.5	1.13
cobalt	10	22		8.0	1.13
(cathode in sheath	10	32	40	4.5	1.12
to prevent slime	10	42		5.5	1.12*
incorporation in the	10	52		5.5	1.11*
cathodic deposit)	30	82		6.5	1.11
	30	112		7.5	1.10
	20	132		7.5	1.10
solution VI					
copper	5	5	20		1
	5	10	10	2.5	0.995
	10	15	10		0.990
cobalt	5	5			0.995
	10	15	40	8.5	0.990
	30	45			0.985

* Electrolyte agitation with the rate of 1180 rpm

electrolysis are summarized in table 1. At the end of each electrolysis stage, samples of the electrolyte were taken, pH was adjusted (during cobalt electrowinning, when necessary) and the cathodic deposits were stripped (copper with 7 M HNO_3, cobalt with 2 M H_2SO_4 + H_2O_2).

2.3. Processing of the slime

A sample of dry slime (42,648 g) was dissolved in 1 dm³ hot 2 M H_2SO_4. pH of the solution (solution IV) was 0.4. To recover copper from acidic solution a series of 1h electrolysis at various current densities (40, 80 and 200 A/m²) and in constant time of 1 h were carried out. However, too high concentration of iron ions in the bath made copper electrodeposition impossible. To remove iron from this solution NaOH was added to reach pH 3.5. The iron precipitate (precipitate II) was filtered and then dissolved in 2 M H_2SO_4 (solution V). After some time, black powder precipitated from the filtrate (precipitate III). The powder was separated and dissolved in 2 M H_2SO_4 (solution VII). 2 dm³ of the filtrate (solution VI) was obtained. 1 dm³ of this solution was acidified with HCl to pH = 2.5 and a series of electrolysis's was carried out for copper recovery. After complete copper electrowinning, the solution was alkalized with concentrated ammonia to pH 8.5, and a series of electrolysis's was conducted in order to recover cobalt. Parameters of all electrolysis stages are summarized in table 1. The electrowinning was conducted in the same experimental circuit as previously (chapter 2.2). The electrolyte samples were taken and the cathodic deposits were stripped at the end of each electrolysis stage for the chemical analysis.

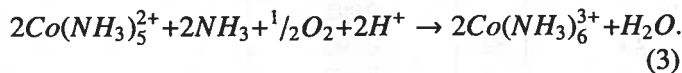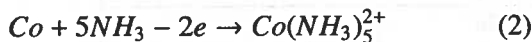## 3. Results and discussion

3.1. Anodic dissolution of alloy

The anodic dissolution of Cu5Co25Fe70 alloy in the ammonia-ammonium chloride solution led to metals transfer to the electrolyte, the formation of the slime and the cathodic deposit. The compositions of all phases and the distribution of each element between them at the end of the dissolution process are given in table 2. The dissolution of Cu5Co25Fe70 alloy in the ammoniacal solution led to the accumulation of all elements mainly in the slime, however about 30% of copper and cobalt codeposited as the alloy. No more than 20% of copper and 15% of cobalt remained in the electrolyte.

TABLE 2

Distribution of metals among phases during anodic dissolution of alloy. Composition of the cathodic deposit, the electrolyte, the slime and Cu5Co25Fe79 alloy

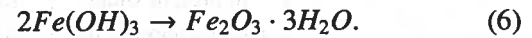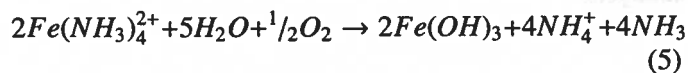| Metal	DISTRIBUTION OF METAL, %			COMPOSITION, wt%			ALLOY COMPOSITION, wt%	
	cathodic deposit	electrolyte	slime	cathodic deposit	electrolyte	slime	calculated	actual
Cu	31.4	20.5	48.1	7.5	22.6	3.8	5.6	5.4
Co	32.2	15.3	52.5	33.5	74.3	18.2	24.7	25.0
Fe	20.1	0.2	79.7	59.0	3.1	78.0	69.7	69.6

The electrolyte contained mainly cobalt and copper ions in the form of ammonia complexes produced in the anodic processes and secondary reactions:

$$Cu + 4NH_3 - 2e \rightarrow Cu(NH_3)_4^{2+} \qquad (1)$$

$$Co + 5NH_3 - 2e \rightarrow Co(NH_3)_5^{2+} \qquad (2)$$

$$2Co(NH_3)_5^{2+} + 2NH_3 + {}^1/_2O_2 + 2H^+ \rightarrow 2Co(NH_3)_6^{3+} + H_2O. \qquad (3)$$

There was some amount of iron in the bath, probably in form of $Fe(NH_3)_4^{2+}$ complexes:

$$Fe + 4NH_3 - 2e \rightarrow Fe(NH_3)_4^{2+}. \qquad (4)$$
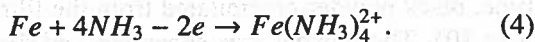
This is confirmed by E-pH diagrams, since they predict stability of ferrous amines in the range of pH = 9.3±1.0 [6]. Moreover, Farrow et al. [7] showed that solubility of iron(II) hydroxide in ammonium chloride solutions with pH above 8 is much more higher than those calculated from the solubility product of Fe(OH)$_2$. The authors stated that there was an evidence for the existence of the iron(II) ammonia complex in the solution. Obviously, the amounts of the iron complexes in the bath were very low, since the precipitation of hydrated oxide occurred immediately in the secondary reactions:

$$2Fe(NH_3)_4^{2+} + 5H_2O + {}^1/_2O_2 \rightarrow 2Fe(OH)_3 + 4NH_4^+ + 4NH_3 \qquad (5)$$

$$2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot 3H_2O. \qquad (6)$$

The iron precipitates drifted in the bath or remained on the anode surface as the slime. The circulation of the iron precipitates in the solution was disadvantageous, since they were incorporated into the cathodic deposit of Cu-Co alloy:

$$Cu(NH_3)_4^{2+} + 2e \rightarrow Cu + 4NH_3 \qquad (7)$$

$$Co(NH_3)_6^{3+} + 3e \rightarrow Co + 6NH_3. \qquad (8)$$
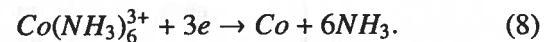
The anodic slime essentially consisted of the iron and cobalt chemical compounds produced in secondary reactions. It seems that coprecipitation of cobalt compound was preceded by the adsorption of Co(NH$_3$)$_6^{3+}$ ions on the iron precipitates [1]. Han et al. [8] showed that the solid product of the coprecipitation of cobalt ions with Fe(III) ions in ammoniacal solution had spinel structure CoO·Fe$_2$O$_3$. Similar conclusions can be drawn from XRD studies of slimes produced during anodic dissolution of Cu-Co-Fe alloy [1]. In the present study the molar ratio of cobalt to iron in the anodic slime was 1:4:

$$\frac{(m_{Co})_S}{M_{Co}} : \frac{(m_{Fe})_S}{M_{Fe}} = 1 : 4, \qquad (9)$$

where: $(m_{Fe})_S$ and $(m_{Co})_S$ – mass of iron and cobalt in the slime, M_{Co} and M_{Fe} are molar masses of iron and cobalt.

Thus, the dry slime is assumed to be a 1:1 mixture of CoO·Fe$_2$O$_3$ and Fe$_2$O$_3$ with low copper content. Copper in the slime originates probably from the adsorption of Cu(NH$_3$)$_4^{2+}$ complexes on the iron compounds. However,

TABLE 3

Composition and Cu:Co:Fe weight ratios in the slime and the alloy

Phase		Composition, wt%			Cu:Co:Fe
		Cu	Co	Fe	
Slime		3.8	18.2	78.0	1 : 4.8 : 20.4
Alloy		5.4	25.0	69.6	1 : 4.6 : 12.9
	Alloy matrix	5.2±1.2	25.1±0.2	69.7±1.4	1 : 4.8 : 13.4
	Alloy precipitate	0.34±0.32	2.7±0.4	97.0±0.2	1 : 9.0 : 323

the E-pH diagram for $Cu-NH_3-Cl-H_2O$ system [9] suggests that $Cu(NH_3)_4^{2+}$ complex can transform into CuO in the dry slime.

The molar ratios of the chemical compounds in the slime are:

$$\frac{m_{CoO\cdot Fe_2O_3}}{M_{CoO\cdot Fe_2O_3}} : \frac{m_{Fe_2O_3}}{M_{Fe_2O_3}} : \frac{m_{H_2O}}{M_{H_2O}} : \frac{m_{CuO}}{M_{CuO}} = 1 : 1 : 1 : 0.2$$
(10)

and the final composition of the dry slime seems to be $CoO\cdot Fe_2O_3 + Fe_2O_3\cdot H_2O$ contaminated with CuO.

The weight ratio Cu:Co:Fe in the slime was calculated and compared with that in the alloy, in the alloy matrix and the in alloy precipitates (Cu5Co25Fe70 alloy is a two phase system [2]). The results of calculations are given in table 3. It is seen that Cu:Co ratio in the slime is similar to that in the alloy and, especially, to that in the matrix. Moreover, the theoretical alloy composition calculated from the total amounts of metals transferred from the anode is the same as the actual alloy composition (table 2). It means that the alloy dissolution was not a selective process and all metals were released from the anode simultaneously. However, very low fraction of the alloy precipitates in the Cu-Co-Fe alloy (estimated as 1.8±1.5 wt.%) made impossible to find out if they remained as a high-iron alloy in the slime (as it was observed during spontaneous dissolution of Cu90Co5Fe5 alloy [1]).

3.2. Processing of the electrolyte

High total volume of the ammoniacal electrolyte produced during the alloy dissolution was reduced by evaporation. It is worth noting, that the evaporation was accompanied by periodical changes of the colour of the solution from violet to green, which is characteristic for $[Co(NH_3)_4Cl_2]^+$ complex in cis (violet) and trans (green) isomer forms. This observation confirmed that cobalt(III) complex ions were present in the ammoniacal solutions. In acidic solutions Co(II) ions are stabilized.

In the concentrated solution a pink-red chemical compound precipitated. Probably, it was cobalt

compound, since the electrolyte contained mainly cobalt ions. It is supposed that the precipitate was cobalt(III)-ammonia chloride $[Co(NH_3)_6]Cl_3$ [10], which is insoluble in water and ammonia solution [11].

Addition of some amount of H_2SO_4 did not dissolve this precipitate, but its volume enlarged (precipitate I). It seems that $[Co(NH_3)_6]Cl_3$ transformed into alum $Co_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot6H_2O$ [10]. It is known, that some cobaltic ammonia complexes exist in strong acidic as well as in strong basic solutions [12]. However, it could not be confirmed by E-pH diagram for $Co-NH_3-H_2O-H_2SO_4$ system [13], since it predicts stability of $3Co(OH)_2\cdot CoSO_4$ at pH 7-8.5 or $CoSO_4\cdot(NH_4)_2SO_4\cdot6H_2O$ at pH 1-7.
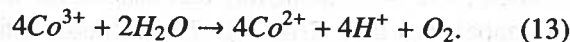
The cobaltic precipitate was dissolved in water. Cobaltic salts are unstable in aqueous solutions and Co^{3+} ions transform fast into Co^{2+} and CoO_2 in disproportionation reaction [12]:

$$2Co^{3+} + 2H_2O \rightarrow Co^{2+} + CoO_2 + 4H^+. \quad (11)$$
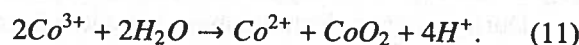
In turn CoO_2 easily oxidizes water with Co^{2+} formation and oxygen evolution:

$$2CoO_2 + 2H_2O \rightarrow 2Co^{2+} + O_2 + 4OH^-. \quad (12)$$
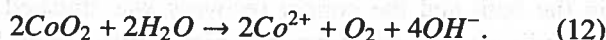
Hence, overall reaction is:

$$4Co^{3+} + 2H_2O \rightarrow 4Co^{2+} + 4H^+ + O_2. \quad (13)$$

Aqueous solution of the precipitate contained 0.6 g Co^{2+} and $2\cdot10^{-3}$ g Cu^{2+} (solution II). After pH adjustment from 2.1 to 9, the electrowinning of cobalt was carried out. The dependence of the cobalt mass in the electrolyte and the cathodic deposit on the electrolysis time is shown in Fig. 2. It is seen that after 19 h the cobalt recovery was completed (the final solution contained only $1.7\cdot10^{-3}$ g Co^{2+}).
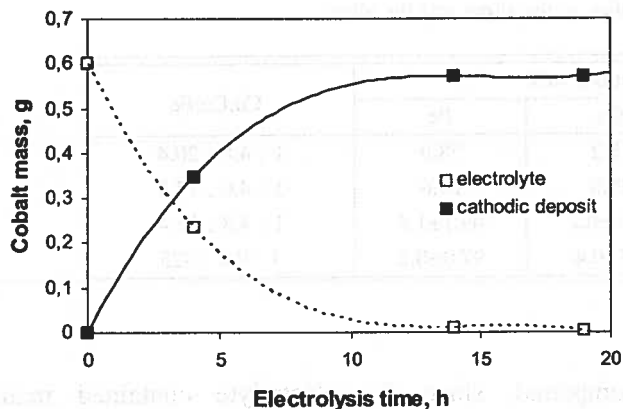
Fig. 2. Recovery of cobalt from solution II – influence of the electrolysis time on cobalt contents in electrolyte and cathodic deposit

The purity of the cobalt cathodic deposits was very high: 99.9% (0.1% Cu) in first stage of the electrolysis and 100% in next one. The current efficiencies were dependent on the cobalt ions concentration in the bath and they decreased linearly from 99.4% after 4 h to 3.7% after 19 h of the process.

2 dm^3 of the evaporated electrolyte (solution III) after anodic dissolution contained 0.472 g Cu^{2+}, 0.951 g Co^{2+} and 0.064 g Fe^{3+}. Since initial pH of the solution was 0, there was a possibility to conduct (by simple pH regulation) electrowinning of metals selectively: copper from acidic solution and then cobalt, after pH adjustment. A sample of 1 dm^3 of the solution III was used for the electrowinning. Obtained results are presented in Fig. 3 and Fig. 4 for copper and cobalt, respectively.

During copper electrowinning a gradual decrease in the mass of Cu^{2+} ions in the electrolyte and corresponding increasing in the mass of deposited copper was observed (Fig. 3a). It is seen that increments of the deposit mass in each subsequent stage decreased as electrolysis was continued. After 16 h only 8,2·10^{-3} g Cu^{2+} remained in the bath and the copper recovery was finished. The cathodic deposit was copper of high purity (about 99%) (Fig. 3b). With decreasing Cu^{2+} ions concentration in the bath, traces of cobalt and iron began to codeposit and consequently, the purity of the copper deposits decreased to 91-94%. However, total mass of the impurities in copper was only 2·10^{-3} g. The cathodic efficiencies were not high, because of low Cu^{2+} ions concentration in the electrolyte. The cathodic efficiency decreased gradually from about 19% to about 3% with the electrolysis time (Fig. 3c).

After copper recovery from the solution III, pH of the electrolyte was adjusted to 3, and cobalt electrowinning was conducted. However, it was not successful, since pH value was too low and cobalt electrodeposition was impossible, in spite of rather high concentration of
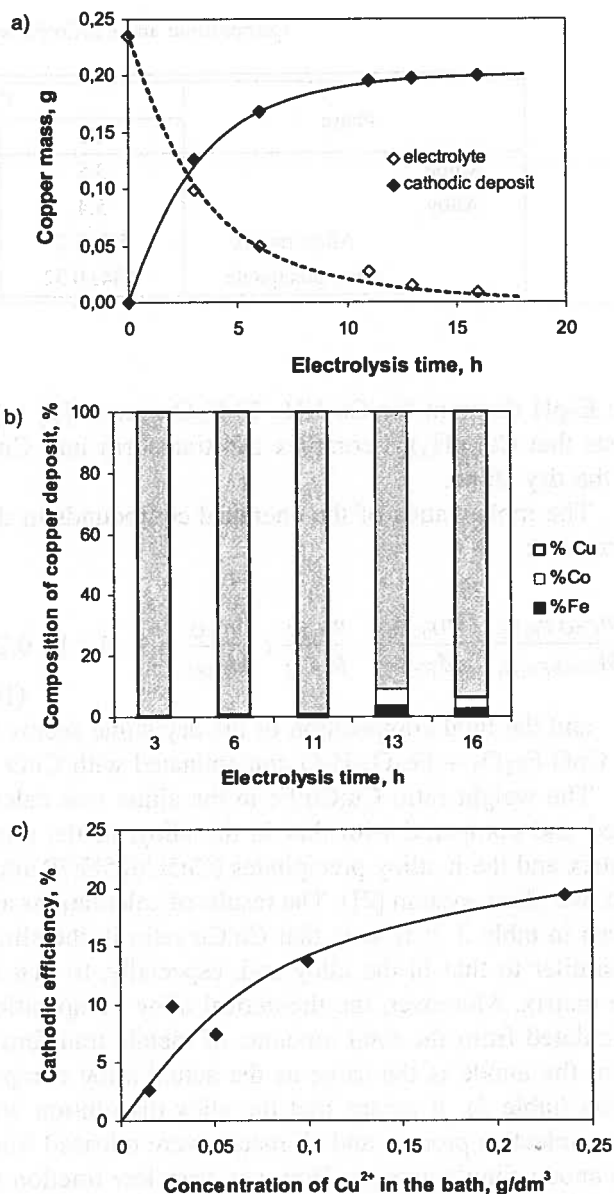

Fig. 3. Recovery of copper from solution III: a) copper content in the electrolyte and the cathodic deposit vs electrolysis time; b) composition of the cathodic deposit vs electrolysis time; c) current efficiency vs concentration of copper ions in the bath

Co^{2+} ions. Instead of it, 1.5·10^{-3} g of copper deposit with some iron was obtained (Fig.4). Therefore, pH was adjusted once more, to 5.5, and then cobalt electrodeposition could proceed. Cobalt was recovered almost entirely from the bath; only 0,3·10^{-3} g of cobalt ions remained in the final solution. The cathodic deposits were Co-Cu alloys with traces of iron. They consisted of 98-99% of cobalt.

The cobalt electrowinning was accompanied by periodical pH adjustment to various levels (table 1). The aim of this test was to find a minimal pH for the cobalt electrodeposition process with satisfactory efficiency. The cathodic efficiencies were very low and the maximum

values were about 3% for pH above 5.5. Nevertheless, it has to be noted that there was concurrent dependence of the efficiency on the concentration of cobalt ions in the bath.
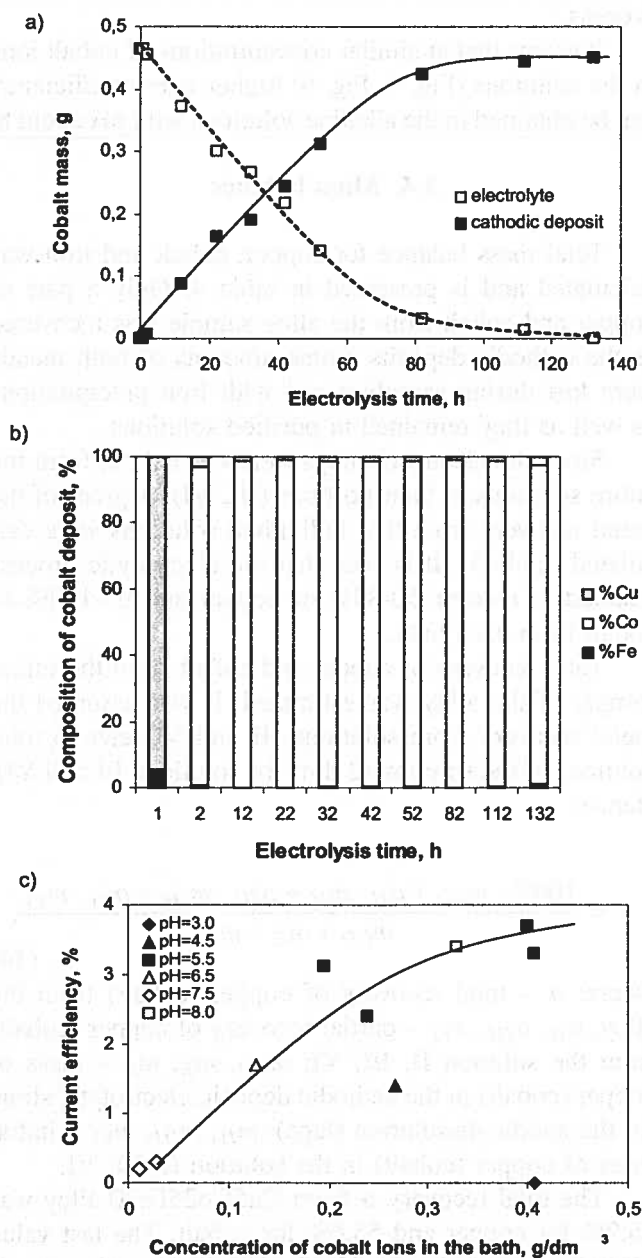

Fig. 4. Recovery of cobalt from solution III: a) cobalt content in the electrolyte and the cathodic deposits vs electrolysis time; b) composition of the cathodic deposit vs electrolysis time; c) current efficiency vs concentration of cobalt ions in the bath and pH

3.3. Processing of the slime

The slime was dissolved in sulphuric acid. The solution (solution IV) contained mainly iron and some cobalt ions as well as little copper ions (table 2). Since pH of it was 0.4, a trial of the selective copper electrowinning was carried out. However, in spite of various applied

current densities, no cathodic deposit was obtained. It is understandable, since the standard reduction potential for Fe^{3+}/Fe^{2+} is 0.77V, whereas that of Cu^{2+}/Cu is 0.34V. Thus, the reduction of Fe^{3+} ions took place first. Moreover, Das and Gopala Krishna [14] showed that copper can be directly electrowon from the acidic electrolytes only when iron contamination is fairly low (less than $1g/dm^3$) and higher current densities (300 A/m²) are used. Hence, iron elimination from the electrolyte is required before copper electrodeposition may take place.

Iron was totally removed from the solution by NaOH addition to pH 3.5. The precipitate (precipitate II) contained 1.7% copper, 15.8% cobalt and 82.5% iron as chemical compounds. No recovery of copper and cobalt was conducted from it.
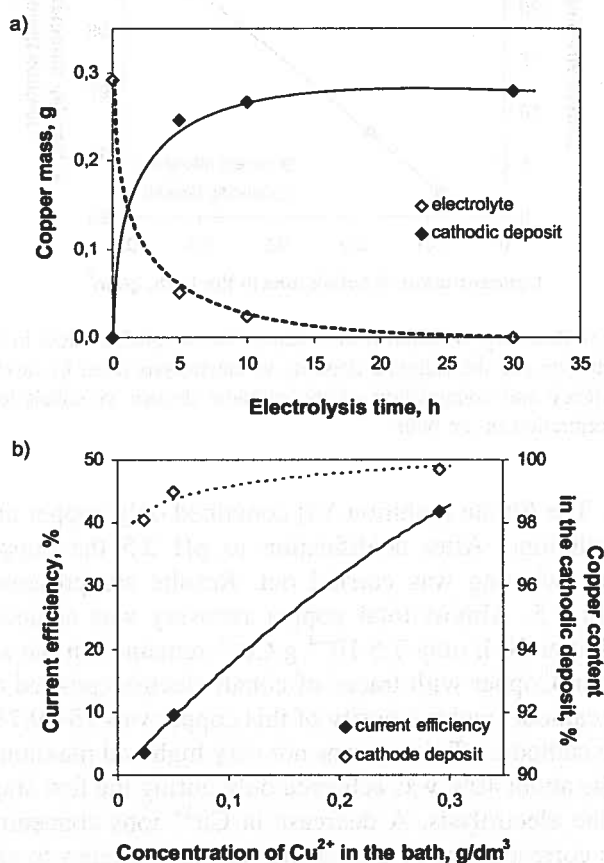

Fig. 5. Recovery of copper from solution VI: a) copper content in the electrolyte and the cathodic deposits vs electrolysis time; b) current efficiency and composition of the cathodic deposit vs copper ions concentration in the bath

After iron precipitate separation from the solution, secondary precipitation took place in the filtrate after 12 h. Black precipitates (precipitate III) were filtered and then dissolved. It contained mainly cobalt (4.8% copper, 93.1% cobalt, 2.1% iron). The precipitate seems to be hydrated cobalt oxide CoO(OH) [10]. No recovery of cobalt was conducted from this solution.
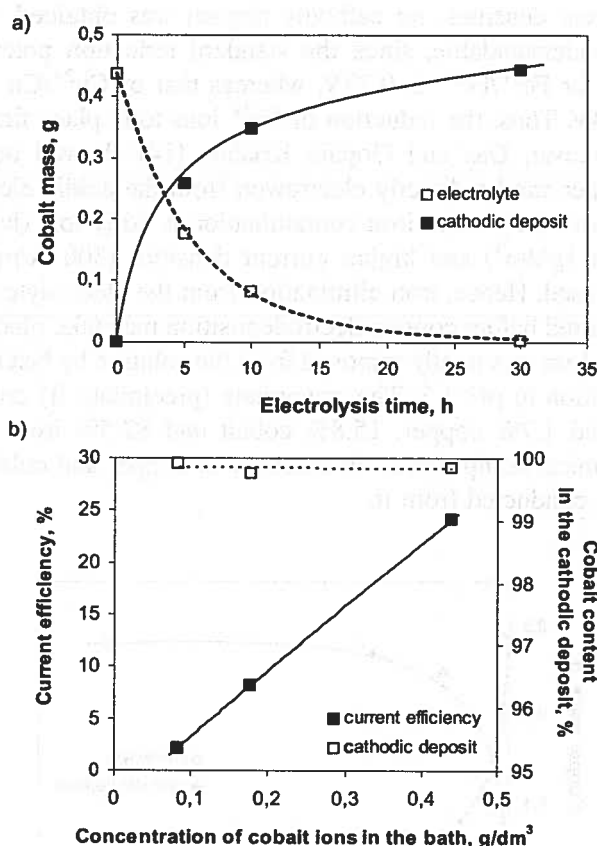
Fig. 6. Recovery of cobalt from solution VI: a) cobalt content in the electrolyte and the cathodic deposits vs electrolysis time; b) current efficiency and composition of the cathodic deposit vs cobalt ions concentration in the bath

The filtrate (solution VI) contained only copper and cobalt ions. After acidification to pH 2.5 the copper electrowinning was carried out. Results are presented in Fig. 5. Almost total copper recovery was achieved and after 30 h only $7.5 \cdot 10^{-4}$ g Cu^{2+} remained in the solution. Copper with traces of cobalt electrodeposited on the cathode, and the purity of this copper was 98-99.7%. The cathodic efficiency was not very high and maximum value about 40% was achieved only during the first stage of the electrolysis. A decrease in Cu^{2+} ions concentration corresponded to decreasing current efficiency to values lower than 10% for Cu^{2+} concentrations below 0.05 g/dm^3.

After copper recovery was completed, pH of the solution was adjusted to 8.5 and the cobalt electrowinning

was carried out. The cobalt recovery was finished after 30 h, when $2.5 \cdot 10^{-3}$ g of cobalt ions remained in the bath (Fig. 6). The purity of the cathodic cobalt was very high, over 99.8%. The maximum current efficiency was 25% and it decreased with time to 2% at the end of the process.

It seems that at similar concentrations of cobalt ions in the solutions (Fig. 4, Fig. 6) higher current efficiency can be obtained in the alkaline solutions with pH about 8.

3.4. Mass balance

Total mass balance for copper, cobalt and iron was calculated and is presented in table 4. Only a part of copper and cobalt from the alloy sample was recovered as the cathodic deposits. Some amounts of both metals were lost during sampling and with iron precipitations as well as they remained in purified solutions.

Since the electrowinnings were carried out from the entire solutions or their portions (III, VI), degrees of the metal recovery from that individual solutions were calculated (table 5). It is seen that the electrolytic process enabled to recover 50-88% of copper and 95-100% of cobalt from each bath.

Total recovery of copper and cobalt from the initial sample of the alloy was estimated. It was assumed the metal recovery from solutions III and VI refer to total volumes of the solution (2 dm^2 for solutions III and VI). Hence:

$$\alpha = \frac{100\% \cdot m_{CD} + \alpha_{II} \cdot m_{II} + \alpha_{III} \cdot m_{III} + \alpha_{VI} \cdot m_{VI}}{m_{CD} + m_E + m_S},$$
(14)

where: α – total recovery of copper (cobalt) from the alloy; α_{II}, α_{III}, α_{VI} – partial recovery of copper (cobalt) from the solution II, III, VI; m_{CD}, m_E, m_S – mass of copper (cobalt) in the cathodic deposit, electrolyte, slime (in the anodic dissolution stage); m_{II}, m_{III}, m_{VI} – initial mass of copper (cobalt) in the solution II, III, VI.

The total recovery α from Cu5Co25Fe70 alloy was 65.9% for copper and 55.6% for cobalt. The last value could be increased to 55.9% if cobalt had been recovered from the solution VII. It is worth to note that about 20% of copper and 42% of cobalt were lost, when iron was removed from the solution IV (as a precipitate II).

TABLE 4

Mass balance for copper, cobalt and iron

Solution	Stage		Mass, g		
			Cu	Co	Fe
	DISSOLVED FROM ALLOY (cathodic deposit + electrolyte + slime)		2.311	10.105	28.469
I	Cathodic deposit		0.726	3.250	5.732
	Electrolyte		0.473	1.551	0.064
II	Initially (in 0.5 dm³)		0.001	0.600	0
	Co electrowinning	recovered	0.0005	0.582	–
		losses in samples	0	0.002	–
		remained in final solution	0.0005	0.002	–
III	Initially (in 2 dm³)		0.472	0.953	0.064
	Cu electrowinning (1 dm³)	recovered	0.201	0.001	0.001
		losses in samples	0.001	0.014	0.001
		remained in final solution	0.008	0.464	0.030
	Co electrowinning	recovered	0.006	0.452	0.001
		losses in samples	0	0.010	0
		remained in final solution	0.002	0.0003	0.001
IV	Slime		1.112	5.304	22.700
V	Iron precipitations		0.461	4.332	22.611
VI	Initially (in 2 dm³)		0.583	0.883	0
	Cu electrowinning (1 dm³)	recovered	0.190	0.001	–
		losses in samples	0.0004	0	–
		remained in final solution	0.008	0.442	–
	Co electrowinning	recovered	0.001	0.442	–
		losses in samples	0	0.001	–
		remained in final solution	0.001	0.003	–
VII	Secondary precipitations		0.007	0.135	0.003

Values lower than 0.0001 g are assumed as 0 g.

TABLE 5

Recovery of copper and cobalt from individual solutions

Solution	Electrowinning stage	Recovery, %	
		Cu	Co
II	Co	50.0*	97.0
III	Cu	85.2	0.3
	Co	2.5	95.0
VI	Cu	65.2	0.2
	Co	0.3	99.8

* It corresponds to 0.5 mg Cu.

quired before the electrowinning in spite of high losses of valuable metals during iron hydroxide precipitation. The high purity cathodic deposits of copper and cobalt were obtained, however the cathodic efficiencies of this process were not high.

The total recovery of copper and cobalt from the alloy was 66% and 56%, respectively. The residual amounts of copper and cobalt remained mainly in the iron precipitates. Some differences in the metal contents in the solution and the cathode deposit were only a few milligrams of a metal.

4. Conclusions

The anodic dissolution of the Cu-Co-Fe alloy in the ammonia-ammonium chloride solution produced Co-Cu alloy as the cathodic deposit and the slime, which was the mixture of $CoO \cdot Fe_2O_3$ + $Fe_2O_3 \cdot H_2O$ oxides with traces of CuO. A certain part of copper and cobalt was accumulated in the ammoniacal electrolyte.

The selective electrowinning of copper and cobalt from the solutions was possible. The slime was dissolved. The removal of iron from the solution was re-

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