Physicochemical Problems of Mineral Processing, 36 (2002), 289-298
Fizykochemiczne Problemy Mineralurgii, 36 (2002) 289-298

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INVESTIGATIONS ON OBTAINING CATHODIC COBALT IN A DIAPHRAGM TYPE ELECTROLYSER

Received March 5, 2002; reviewed and accepted May 15, 2002

The investigations on cobalt electrolysis from cobalt chloride solutions while using diaphragm electrolyser have proved that: 1) Electrodeposition of cobalt should be carried out from solutions, where the pH value ranges from 5.1 to 5.3; the cathode cobalt obtained under those conditions was solid metal, bright and glossy; the current efficiency of the cathode process was 98%. 2) Three stages can be distinguished in the course of electrolytic cobalt deposition from $CoCl_2$ solutions. Stage I – slight changes in the pH value of the catholyte solutions, duration this stage depends an cobalt concentration in the solution. Cobalt obtained during this stage adheres very well to the cathode, its survace is smooth and glossy. Stage II – rapid decrease of pH in the catholyte and first hydrogen bubbles appar (pH≅3.0). Stage III – the electrolysis proceeds with a continuous but small decrease of the catholyte pH value; the cathode deposit begins to come off the ground, it is dark and full of pits;. the current efficiency of the process drops to about 90%. 3) Electrolyser modification by introducing buffer compartments that separate catholite from the anolyte makes possible to extend the stage I of electrolysis which is the most favourable stage in the whole process of cobalt deposition.

Key words:

INTRODUCTION

Cobalt is a metal correlated for years with the growth of the armaments industry and aeronautics. Over the last decade of the previous century new applications of this metal emerged. Cobalt is a component of modern aluminum – nickel alloys applied in high-reliability equipment, as well as of special-purpose corrosion resistant alloys (Curwick et al., 1980; Papp,1988; Charewicz et al., 1998). Considerable quantities of cobalt are necessary in manufacturing of cobalt-nickel batteries, compact discs, audio- and video-tapes. Cobalt is also a catalyst to numerous chemical reactions.

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The main source of metallic cobalt is electrlytic process developed in the early fifties of the last century. (Mantel, 1965; Redden and Greaves, 1992) However the knowledge of basic phenomena in the process of cathode separation of cobalt is still incomplete (Jeffrey et al., 2000). This relates in particular to the process of electrolytic separation of cobalt from chloride solutions. According to the literature reports (Chikovani 1996) certain pyrometallurgical processes can be effectively substituted in the cobalt winning technology by chloro-hydrometallurgical operations. One example is the industrial complex “Norylskij Nikiel”, where leaching of nickel matte containing cobalt by hydrochloric acid was introduced. Having first removed copper and nickel from such chloride solutions, cobalt carbonate or cobalt hydroxide is precipitated, which after dissolution in sulfuric acid, produces an electrolyte solution for use in the process of cobalt cathode deposition.

Therefore the purpose of the present work is investigation of the cobalt electrowinning directly from the cobalt (II) chloride solutions in a diaphragm type electrolyser.

EXPERIMENTAL

DIAPHRAGM ELECTROLYSER

The electrolyser used in the present work is a modified version of a large scale laboratory electrolyser that was used earlier to obtain copper and nickel in the electrolytic process (Łętowski et al., 1979; Adamski et al., 1981). Cathode and anode compartments were in form of modules made of polyamide and suitably sealed. They were separated from each other by porous diaphragms of vacuum-moulded PVC. Circulation of catholyte and anolyte was forced by two peristaltic pumps. Catholyte and anolyte circulated in a closed cycle between the catholyte and anolyte tanks and the cathode and anode compartments respectively, through the inlet connections (placed under the modules) and outlet connections (in the upper part of modules). The electrolyser was powered from DC power supply type *SEL-1*. Ammeter and voltmeter type *ML-1* were used to measure the electrolyser current flow and voltage drop.

Cathodes, 85 x 85 mm, of mat sheet nickel, and lead anodes containing 7% Sb, were hung on copper bars that rested on rails connected to the DC power supply. Cathode current density was 150 A/m^2. Current efficiency of the cathode process was calculated from the mass of cobalt deposited on the cathode.

CATHOLYTE AND ANOLYTE

Catholyte was prepared of pure cobalt(II) chloride. Magnesium oxide (MgO, pure) and hydrochloric acid were used to control the acidity of the catholyte solution. The 1M sodium sulfate solution was used as the anolyte.The pH of the solutions was measured using *R-10* electrodes and a pH-meter (*Digital pH Meter PM-1)*. Catholyte volume was ranging from 750 to 900 cm^3, and the anolyte volume from 900 to 1000 cm^3. In order to effectively limit the chlorine evolution on the anode, a slight penetration of anolyte into the catholyte solution was forced in the following way:

- by using as the anolyte the 1M Na_2SO_4 with the respect to that, that its density (1.125 g/cm^3) is higher than the catholyte solution density which varied between 1.090 and 1.08 g/cm^3, depending on $CoCl_2$ concentration,
- setting mutually different flow values for circulation of anolyte and catholyte through the electrolyser compartments; the anolyte flow was 3.7 cm^3/s, and the catholyte flow was 3.0 cm^3/s.

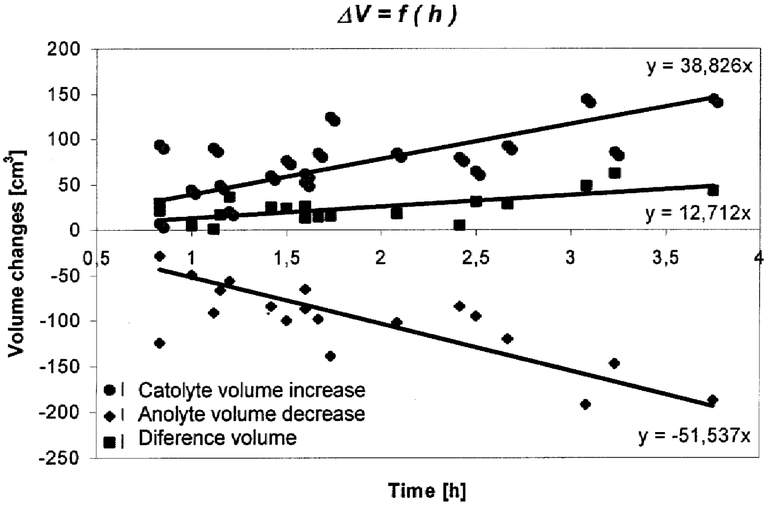


Fig. 1. atholyte and anolyte volume changes during the electrolysis process

To check the effectiveness of the above mentioned efforts, anolyte and catholyte volumes were measured before and after each electrolysis experiment. The measurements of the catholyte and anolyte volume after every one of 18 electrolysis experiments, where each of experiments took 75 to 155 minutes, showed that the catholyte volume after electrolysis was greater than that before the experiment. The diagrams of the catholyte volume increase and of the anolyte volume decrease versus time of electrolysis have been shown in Fig. 1. The constant difference of 24.6% was observed between the anolyte volume decrease and the catholyte volume increase, which is the effect of changing mass and density of the catholyte solution in the course of electrolysis. It can be concluded from the curves presented in Fig. 1, that 51.5 cm^3 (mean value) of anolyte penetrates into the catholyte within one hour.

RESULTS AND DISCUSSION

According to the Pourbaix diagram for the Co – H_2O system (Pourbaix, 1966), the reversible electrode potential for cobalt, in a solution containing cobalt ions at the concentration of 1.0 mole/dm^3 is –0.277 V. This potential in a solution at pH < 4.5 is lower than the electrochemical hydrogen ion reduction potential. Therefore the electrolytical separation of cobalt from solutions at pH < 4.5 shall always proceed with a evaluation of hydrogen. It can be found a very narrow pH range, between 4.5 and 6.2 where the reversible electrode potential for cobalt:

$$Co^{2+} + 2e = Co \tag{1}$$

is higher then the electrochemical potential corresponding to the equilibrium of the hydrogen ion reduction to hydrogen:

$$2H^{+} + 2e = H_2 \tag{2}$$

Within the specified pH range the pure cathode cobalt is winning from solutions of its salts. Therefore there are reports in the literature that the cobalt electrolysis should be run from weak-acid or neutral solutions (Das and Subbaiah, 1984). However, the Das and Subbaiah’s examinations have shown that running the electrolysis of the cobalt sulfate solution, at pH equal to 6.8, in the electrolyser where the cathode space and anode space are not separated, the pH of the bath falls abruptly to pH equal to 4 already within the first 10 minutes. After 120 minutes the pH reaches value 2. Increased electrolyte acidity is the result of reaction taking place on the anode:

$$2H_2O = O_2 + 4H^{+} + 4e \tag{3}$$

Such strong increase of the electrolyte acidity effects in significant reduction of the current efficiency of the process. According to the data obtained by Das and Subbaiah, when the pH value of the solution is 2.0, the current efficiency value reaches 86%, while the pH value lowers to 1.25, the current efficiency drops rapidly to 60%. Owind to use of a diaphragm electrolyser, it was possible to limit the acidity increase in the catholyte.

pH CHANGE IN ANOLYTE AND CATHOLYTE DURING THE ELECTROLYSIS

During the electrolysis the anolyte as well as catholyte pH was measured. The apprpriate values shown in Fig. 2 and Fig. 3. The pH values presented in Fig.2 are the mean values obtained from 10 electrolysis experiments. The anolyte pH value drops rapidly within the first 15 minutes from 5.0 to 2.5. After 1 hour in the electrolysis, the anolyte pH value is 2.1, after 2 hours – it decreases only by 0.2, and reaches 1.9.

The curves presented in Fig.3 shown how the pH values of the catholyte solution depeds on time of electrolysis, the pH value and cobalt concentration in the solution before the electrolysis (see Table 1). Inotial pH values and the cobalt concentration in electrolysed solutions have been given in Table 1.

Table 1. Initial pH value and cobalt concentration in catholyte

Number of electrolysis	pH	[Co] g/dm^3
1	5,16	51,0
2	5,16	33,0
3	5,31	29,9
4	5,53	18,6
5	5,00	40,8
6	4,97	31,0
7	4,90	21,5
8	3,40	40,8

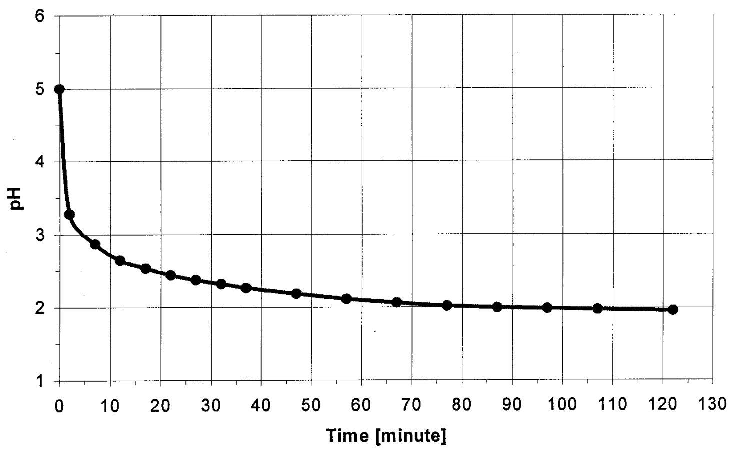


Fig. 2. Anolyte pH changes in the course of electrolysis process

Going through the results presented in Fig. 3 one can observed three cases:

1. *The pH value of the catholyte solution before electrolysis is ranged from 5.2 to 5.5.* Three stages can be distinguished on the curves showing how the pH value changes with the progress of electrolysis:
   Stage I: only slight changes in the pH value of the catholyte solution is observed,
   Stage II: rapid increase in the concentration of hydrogen ions in the catholyte solution (pH is falling); such situation will develop when the catholyte pH value during the electrolysis decreases to somewhere near 4.9.
   Stage III: small but continuous increase of the catholyte acidity.
2. *The pH value of the catholyte solution before electrolysis is ranged from 4.5 to 4.9;* stage I, does not show on the curves of pH value versus time electrolysis, in stage II the decrease of the pH value is much more extended in time compared with the stage II for the first case, stage III shows very small but continuous increase of the catholyte acidity.

3. *The pH value of the catholyte solution before electrolysis is ranged from 3.2 to 3.5;* the catholyte pH value versus time of electrolysis show a continuous, slight decrease; the stage I and II is not observed.

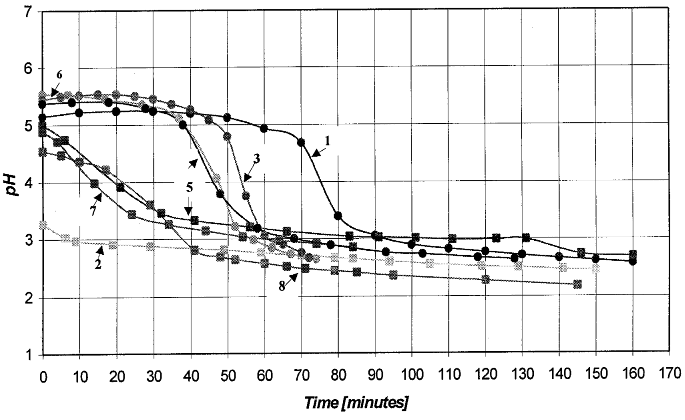


Fig. 3 .Catholyte pH changes versus time of electrolysis, initial pH value and cobalt concentration in catholyte (current density 150 A/m^2)

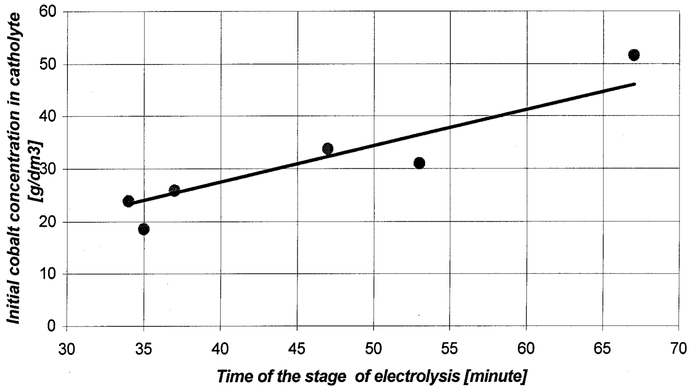


Fig. 4. Effect of initial cobalt concentration in catholyte on duration of the stage I of electrolysis (current density 150 A/m^2)

It was found that the duration of the stage I of electrolysis depends on cobalt chloride concentration in the catholyte solution. The higher initial cobalt concentration in the solution, the longer time of stage I of the electrolysis is observed. The relation has been presented in Fig.4.

HYDROGEN EVOLUTION

The first hydrogen bubbles appear on the cathode when the catholyte pH value drops to about 3.0 (stage III of the electrolysis). The starting point of the hydrogen evolution was manifested by a slight but noticeable voltage increase in the electrolyser. That phenomenon was observed in each electrolysis experiment. Relation between the voltage on the electrolyser and the duration of electrolysis, for two selected electrolysis experiments has been presented in Fig.5. The difference between the voltage values just before, and just after the hydrogen evolution had started, was 0.1 V. The moment of hydrogen appearance depends on the duration of the stage I of the electrolysis, and thus on the pH value of and cobalt concentration in the solution before the electrolysis. The relevant relation has been shown in Fig.6.

Fig. 5. Voltage change on electrolyser versus time of electrolysis

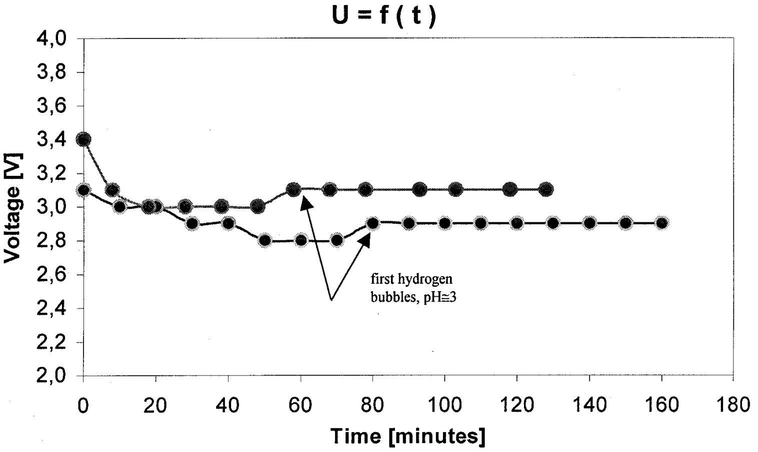
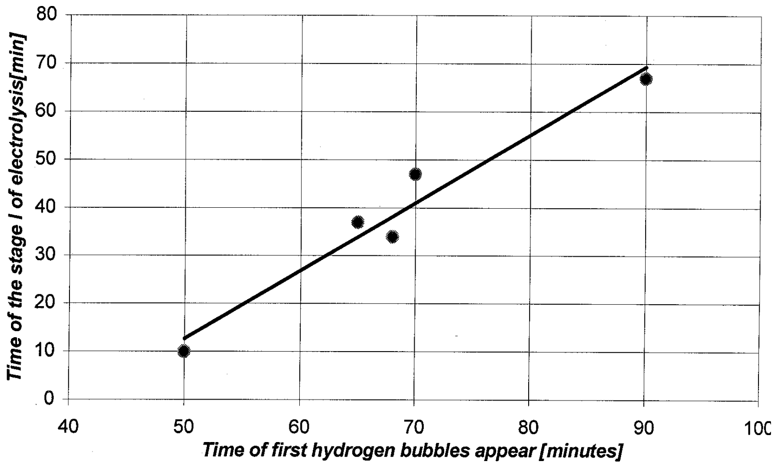


Fig. 6. Effect of the electrolysis stage I duration on the time of appearing the first hydrogen bubbles



CATHOLYTE PH EFFECT ON THE CURRENT EFFICIENCY AND ON THE CATHODE COBALT QUALITY

To determine the catholyte pH effect on the current efficiency and the quality of the cathode cobalt, the diaphragm electrolysis was carried out when using a cobalt chloride solution of pH equal to 5.16 and containing 51 g of Co in 1 dm^3. Cobalt was deposited on matted nickel electrodes. The pH of the catholyte solution was monitored in the course of electrolysis. When the pH value reached 3.0, the cathodes were removed from the solution, washed carefully and dried. They were replaced by nickel cathodes plated with a thin layer of cobalt. Duration of electrolysis before the replacement of cathodes (total time of the stage I and II) and after the replacement of cathodes (stage III) was the same, 80 minutes. Four such experiments of electrolysis were carried out. The mean current efficiency was calculated from the cathodes mass increment. The mean current efficiency corresponding to the stage I and II was 97.2%. In case of electrolysis run from the solutions of $pH < 3$ (the stage III), the mean current efficiency was 90.1%. Cobalt obtained during the electrolysis from $CoCl_2$ solutions of pH ranging from 5.16 to 3.0 adhered very well to the cathode. Its surface was smooth, bright and glossy. In case of electrolysis from solutions of pH less than 3.0, cracks could be seen on the cathode deposit layer, the surface of the deposit was dull, dark and full of pits. Those pits were the spots of hydrogen bubbles formation.

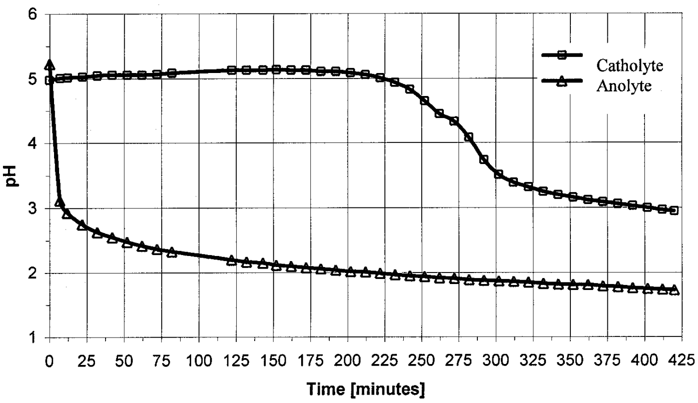


Fig. 7. pH changes in anolyte and in catholyte in the course of diaphragm electrolysis after introducing buffer compartments

DIAPHRAGM ELECTROLYSIS WHEN INTRODUCING A BUFFER COMPARTMENT

The investigations presented above indicate that obtaining the electrolytic cobalt from chloride solutions is most efficient if the initial pH of the catholyte ranges from 5.16 to 5.45, and during the electrolysis remains fixed (see Fig.3). Therefore efforts ought to be made to limit anolyte penetration into the catholyte solution, and thus to limit the catholyte acidification. It can be done by introducing buffer compartments that separate the cathode compartments from the anode ones. The buffer compartments were filled with 1M Na_2SO_4 solution. The electrolyte in the buffer compartments was maintained still. Circulation flows of anolyte as well as catholyte were the same as in case of electrolysis run without buffer compartments. The cathode current density was 150 A/m^2. Initial cobalt concentration in the catholyte solution was 59.8 g/dm^3, and the pH value of the solution was equal 5.16. The pH changes in the catholyte and in the anolyte solutions during the electrolysis have been shown in Fig.7. The time interval of when the pH value remains constant is threefold longer as compared with the time of the stage I of electrolysis run without buffer compartments. The obtained cathode cobalt was pure metal, bright and glossy. The current efficiency of the cathode process was 98%. It needs be mentioned that the modification of the diaphragm electrolysis process by introducing buffer compartments requires further investigation on possible reduction of resistance of the total system. This parameter value decides on the consumption of energy during this process.

CONCLUSIONS

The investigations on cobalt electrolysis from cobalt chloride solutions while using diaphragm electrolyser have proved that:

1. The pH value of the catholyte solution is a critical parameter and it effects the quality of cathode cobalt and the current efficiency of the process.
2. Electrodeposition of cobalt should be carried out from solutions, where the pH value ranges from 5.1 to 5.3; the cathode cobalt obtained under those conditions was solid metal, bright and glossy; the current efficiency of the cathode process was 98%.
3. Hydrogen starts to evolve when the catholyte pH drps to about 3.0; the quality of cobalt being deposited on the cathode becomes worse, and the current efficiency decreases.
4. Three stages can be distinguished in the course of electrolytic cobalt deposition from $CoCl_2$ solutions:
    - Stage I: typical for this stage of elecrolysis are only slightly changing in the pH value of the catholyte solution as compared with the initial pH value equal 5.2÷5.5; duration of the this stage I depends on cobalt concentration in the solution; cobalt obtained during this stage of electrolysis, adheres very well to the cathode, its surface is smooth and glossy.
    - Stage II: rapid decrease of pH value in the catholyte and first hydrogen bubbles appear. Evolving hydrogen (by $pH<3.0$) causes a slight voltage increase on electrolyser.
    - Stage III: the electrolysis proceeds with a continuous but small decrease of the catholyte pH value; the cathode deposit begins to come off the ground, it is dark and full of pits;. the current efficiency of the process drops to about 90%.
5. Electrolyser modification by introducing buffer compartments that separate catholyte from the anolyte makes possible to extend the stage I of electrolysis which is the most favourable stage in the whole process of cobalt deposition. The experiments carried out after the buffer compartments had been implemented, the time interval of the stage I of electrolysis was threefold longer as compared with the time attained previously in the process of diaphragm electrolysis.

REFERENCES

ADAMSKI Z., CHMIELEWSKI T., ŁĘTOWSKI F., (1981*) Recovery of nickel from used catalysts,* Rudy Metale, 26, 252 – 54.

CHAREWICZ W., CHMIELEWSKI T., WALKOWIAK W., (1998), *in III Seminar of Cobalt,* May Lubin,.

CHIKOVANI A.A., (1996), *Several problems of production of non ferrous metals,* Tsvetnye Metally, 5, 69 – 70.

CURVICK L.R., PETERSON W.A., AND MAKAR H.V., (1980), *Availability of critical scrap metals containing chromium in the Unites States. Superalloys and cast hest – and corrosion – resistant alloys.* US Bur. Mines IC 8821, 51 pp.

DAS S.C., SUBBAIAH T., (1984), *Electrowinning of cobalt. I. Winning from pure cobalt sulphate bath, Hydrometallurg*y, 12, 317 – 333.

JEFFREY M.I., CHO W.L., BREUER P.L., (2000), *The effect of additives and impurities on the cobalt electrowinning process,* Minerals Eng., vol. 13, No. 12, 1231 – 1241.

ŁĘTOWSKI F., KOŁODZIEJ B., CZERNECKI M., JĘDRCZAK A., ADAMSKI Z., (1979), *New hydrometallurgical method for the processing of copper concentrates using ferric sulphate,* Hydrometallurgy, 4, 169 – 184.

MANTEL C.L., (1960), *Electrochemical Engineering,* Mc Graw – Hill Book Company, Inc.

PAPP J.F., (1988), Superalloy recycling 1976 – 1986, In: S. Reichman, D.N. Duhl, G. Maurer, S. Antolovich and C. Lund (Editors), Superalloys 1988. Metall. Soc. AIME, Warrendale, Pa., pp. 367 – 376.

POURBAIX M., (1966), *Atlas of electrochemical equilibria in aqueous solutions,* Pergamon Press.

REDDEN L.D., GREAVES J.N., (1992), *The technical and economic aspects of producing high – purity cobalt and nickel from superalloy scrap utilizing a duble – membran electrolytic cell,* Hydrometallurgy, 29, 547 – 565.

Kołodziej B., Adamski, Z., Włodek T., *Badania nad otrzymywaniem kobaltu katodowego przy zastosowaniu elektrolizera przeponowego, Fizykochemiczne Problemy Mineralurgii, 36, 289-298 (w jęz. ang.)*

Badania nad elektrolizą kobaltu z roztworów chlorku kobaltu w elektrolizerze przeponowym wykazały, że: 1) Elektrowydzielanie kobaltu należy prowadzić z roztworów, których pH wynosi od 5.1 do 5.3; otrzymany w tych warunkach kobalt katodowy był lity, jasny i błyszczący; wydajność prądowa procesu katodowego wynosiła 98%. 2) Podczas elektrolitycznego wydzielania kobaltu wyróżnić można trzy etapy. Etap I charakteryzuje się nieznacznym wzrostem pH; czas trwania tego etapu zależy od stężenia kobaltu w roztworze; wydzielony kobalt ściśle przylega do katody, jest gładki i błyszczący. Etap II to gwałtowny spadek pH katolitu i pojawienie się pierwszych pęcherzyków wodoru (pH≅3.0). Etap III – elektroliza przebiega przy ciągłym, niewielkim, zmniejszaniu się pH katolitu; kobalt katodowy zaczyna odstawać od podłoża, jest ciemny z licznymi wgłębieniami; wydajność prądowa spada i wynosi 90%. 3) Stwierdzono, że zmiana konstrukcji elektrolizera polegająca na wprowadzeniu przestrzeni buforowych, oddzielających katolit od anolitu pozwala na wydłużenie I etapu elektrolizy, który jest najkorzystniejszy dla procesu wydzielania kobaltu.