

## Investigations of composite coatings used as anodes for zinc electroextraction from sulphate electrolytes

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New anodic materials used as anodes for zinc electroextraction have been investigated. These materials are composite coatings, deposited on lead-calcium rolled substrates, consisting of a lead matrix and a cobalt-titanium phase. The cobalt and titanium are presented in the lead matrix as CoTiO<sub>3</sub> nanoparticles. The behaviour of lead-cobalt-titanium anodes during zinc electroextraction is studied by means of galvanostatic polarization investigations. The processes, occurring on the anodes during zinc electroextraction, are studied by cyclic voltammetry. The surface morphology of composite electrodes is investigated by scanning electron microscopy (SEM).

It has been established that the anodic potentials of the composite electrodes investigated are negligibly higher than those of the classical lead-silver alloy. It has been shown by cyclic voltammetry that the curves of the new electrodes possess the same characteristic peaks as those of pure lead and lead-silver electrode.

**Key words:** zinc electroextraction, composite coatings, cobalt, titanium.

### INTRODUCTION

Cast Pb-Ag anodes with silver content of 0.8–1% have been currently used for zinc electroextraction from sulphate electrolyte solutions under industrial conditions. The good characteristics of those anodes have determined their general application. However, the investigations, aiming at improving their technical and economical parameters, namely – corrosion resistance, electrocatalytic properties, conductivity, mechanical indices, price, etc. – as well as the continuous search for alternative anodes, have never ceased. Alloys with a wide range of component concentration with the aim of finding the optimum content of the anode alloy, as well as the electrochemical catalytic role of the elements and the modifying and the structural factors, are being studied. A great part of the investigations have been connected with the utilisation of Co as an alloying component of the lead anodes, mainly because of its significant catalytic effect on the main anode reaction ( $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}$ ). The inclusion of Co in the lead matrix has been carried out in several different ways using various cobalt compounds, namely – metallurgical alloying, metallic-ceramic scorching, detonation deposition of cobalt onto the lead, electrochemical deposition of lead-cobalt-alloy or composite coatings, etc. [1–7].

As compared to the classical Pb-Ag anodes, the Co-containing anodes possess a higher corrosion resistance, a decreased anode polarization as well as a considerably diminished slime formation. At the same time, however, with them a certain unstability of the indices with time has been reported, namely – chemical and electrochemical solubility, mainly, leading to a decrease of the cathode – current efficiency as regards zinc, or even, to its reverse dissolution. Despite the above disadvantages, however, the investigations in developing cobalt-containing anode materials prove to be worthwhile, so that those materials should retain all the qualities of the cobalt catalysts, while at the same time they should stay chemically and electrochemically stable to prevent the harmful effect of the cobalt ions on the cathode process.

The present paper has emerged as a continuation of our research on obtaining anode materials on the basis of the composite lead-cobalt coatings (of the type Pb/Co<sub>x</sub>Me<sub>y</sub>O<sub>z</sub>) on lead-alloy substrates with nanodimensions of the disperse particles.

### EXPERIMENTAL

The new anodic materials have been obtained by electrodeposition onto lead-calcium (Pb-Ca0.089%) 20×20 mm plates. The pre-treatment of the lead substrates included degreasing and chemical etching. The composite coatings were electrodeposited from a lead ammonium sulphamate electrolyte (LASE) containing: 150 g·l<sup>-1</sup> Pb(SO<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>, 100

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$\text{g}\cdot\text{l}^{-1}$   $\text{NH}_4\text{SO}_3\text{NH}_2$  and  $50 \text{ g}\cdot\text{l}^{-1}$  free  $\text{HSO}_3\text{NH}_2$   $0.2 \text{ g}\cdot\text{l}^{-1}$  glue as well as Co and Ti in the form of  $\text{CoTiO}_3$  at a concentration in the electrolyte  $5 \text{ g}\cdot\text{l}^{-1}$ , were added. The electrodeposition was carried out at pH values 1.10; at cathodic current density  $i_c = 1 \text{ A}\cdot\text{dm}^{-2}$  and magnetic stirring. The average thickness of the  $\text{Pb-CoTiO}_3$  composite coatings was  $60 \mu\text{m}$ . The new anodic materials were studied by microprobe X-ray analysis, galvanostatic polarization investigations, cyclic voltammetry (CVA), atomic absorption analysis and scanning electron microscopy.

## RESULT AND DISCUSSION

### Galvanostatic polarization investigations

Galvanostatic polarization investigations have been employed with the aim of determining the anodic potential alteration as a function of time during the process of electroextraction of zinc from sulphate electrolytes. A model electrolyte was used, containing  $55 \text{ g}\cdot\text{l}^{-1}$   $\text{Zn}^{2+}$  (as  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ ),  $180 \text{ g}\cdot\text{l}^{-1}$   $\text{H}_2\text{SO}_4$  and  $5 \text{ g}\cdot\text{l}^{-1}$   $\text{Mn}^{2+}$  (as  $\text{MnSO}_4\cdot\text{H}_2\text{O}$ ). The work electrodes (anodes) were  $\text{Pb-Co}1.22\%\text{-Ti}2.48\%$  and  $\text{Pb-Co}1.13\%\text{-Ti}1.72\%$ . Their effective area was  $2 \text{ cm}^2$ . The cathodes represented two aluminium plates with a total working area equal to that of the anode. The reference electrode was  $\text{Hg/Hg}_2\text{SO}_4$  (SSE) with a potential  $E_{\text{SSE}} = +0.692 \text{ V}$  (NHE), while the temperature during the electroextraction was kept constant at  $37\pm 1^\circ\text{C}$ .

The alteration of the anodic potential as a function of the time for the composite electrodes is given in Fig. 1. The  $\text{Pb-Co}1.22\%\text{-Ti}2.48\%$  (curve 1) and the  $\text{Pb-Co}1.13\%\text{-Ti}1.72\%$  (curve 2) electrodes have exhibited a difference in the anodic potential of approximately 30–40 mV. The  $\text{Pb-Co}1.22\%\text{-Ti}2.48\%$  electrode, where the Co and Ti content is higher, has a lower potential than that of the  $\text{Pb-Co}1.13\%\text{-Ti}1.72\%$ -electrode, which is, eventually, due to the larger area of the anode during polarization [8]. The composite electrodes have exhibited a negligibly higher anode potential as compared with the cast  $\text{Pb-Ag}1\%$  (curve 3). The slime formation with the composite electrodes is much less and the electrolyte after the electro-extraction is clearer and more transparent compared with the standard  $\text{Pb-Ag}1\%$  electrodes.

The atomic absorption analysis of the electrolyte after the electroextraction has shown that the  $\text{Co}^{2+}$ -ions content in it does not exceed 1 ppm. This fact indicates that the composite electrodes possess a good corrosion resistance.

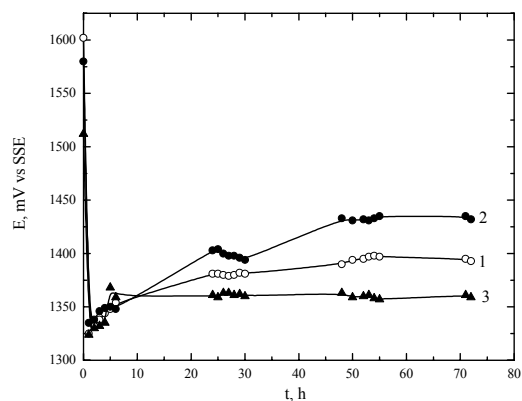


Fig. 1. Dependences of anodic potential on time. 1 -  $\text{Pb-Co}1.22\%\text{-Ti}2.48\%$ ; 2 -  $\text{Pb-Co}1.13\%\text{-Ti}1.72\%$ ; 3 -  $\text{Pb-Ag}1\%$  - cast alloy.

### Cyclic voltammetry

The anode oxide film, formed on the boundary with the electrolyte, is of paramount importance to the work durability of the lead-alloy anodes during zinc electroextraction [9]. Consequently, cyclic voltammetry investigation has been applied in studying this layer on composite anodes, formed in galvanostatic polarization  $i_a = 5 \text{ A}\cdot\text{dm}^{-2}$  in the course of 0, 24 and 48 hours. The electrolyte used is the same as in the previous galvanostatic investigations. The anode area is  $1 \text{ cm}^2$ , the cathode is an aluminium plate with the same area, while the reference electrode is the same as that, used in previous studies. The investigation was carried out at room temperature.

Figure 2 has presents the CVA-curves for the  $\text{Pb-Co}1.22\%\text{-Ti}2.48\%$ -electrode. The scanning of the potential has been done from  $-1.4 \text{ V}$  (SSE) to  $+1.9 \text{ V}$  (SSE) at a sweep rate of  $10 \text{ mV}\cdot\text{s}^{-1}$ . Curve 1, obtained immediately after immersing the anode in the electrolyte has registered two characteristic anodic and two characteristic cathodic peaks, described by Yamamoto *et al.* [10]. The first anodic peak (a) is related to the reaction  $\text{Pb} \rightarrow \text{PbSO}_4$ . Then a well-shaped and stable passive region has been established where the anode layer consists mainly of  $\text{PbSO}_4$  and tet- $\text{PbO}$  (tetragonal), while small amounts of  $\text{PbO}\cdot\text{PbSO}_4$ ,  $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$  and orthorhombic  $\text{PbO}$  may be present as well. Then,  $\text{PbO}_2$  formation (peak b) and oxygen evolution follow. In this case  $\beta\text{-PbO}_2$  has been formed only, since the reduction peak (c) has not been split into two [11]. The splitting of the latter is, probably, due to the presence of two phases –  $\alpha$ - and  $\beta\text{-PbO}_2$ . That same peak is connected with the reduction of  $\text{PbO}_2$  to  $\text{PbSO}_4$ . Peak (d) is determined by the process of

$\text{PbSO}_4 \rightarrow \text{Pb}$ . After 24 hours of polarization, the cyclic voltammogram has indicated several peculiarities (curve 2). The first anodic peak (a) is a bit higher and slightly shifted in the positive direction. In the region of the second anodic peak (b) the curve is shifted in the negative direction, which can be accounted for by the catalytic effect of Co and the roughness of the anodic surface. The reduction peak (c) is well formed. After 48 hours of polarization (curve 3), a well-defined high lead-sulphate peak (a) has emerged. The second anodic peak (b) has overlapped the same peak in curve 2. The appearance of a new anodic peak (b') at approximately +0.9 V (SSE) has emerged as a characteristic feature. This peak has been described by Yamamoto *et al.* [10] and is related to the oxidation of Pb to  $\text{PbSO}_4$  through the  $\text{PbO}_2$ -pores, i.e. it appears only in the presence of the formed  $\text{PbO}_2$  on scanning the potential in the negative direction.

Figure 3 presents the CVA-dependences for sample Pb-Co1.13%-Ti1.72%. The characteristic anodic and cathodic peaks, registered in the previous figure, are evident here as well. The peaks in this case have a lower current value compared to Fig. 2. Moreover, after 24 hours of polarization a new anodic peak (a') has appeared, which is due to the formation of lead oxisulphate –  $\text{PbO} \cdot \text{PbSO}_4$  [9].

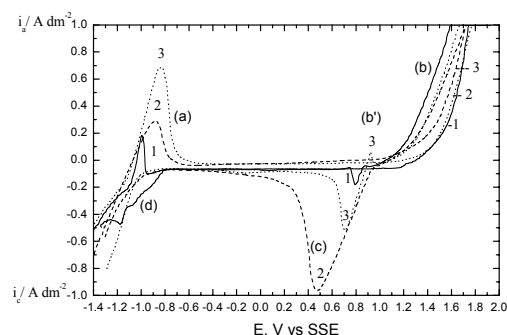


Fig. 2. CVA for a Pb-Co1.22%-Ti2.48%: 1 - 0 h polarization; 2 - 24 h polarization; 3 - 48 h polarization.

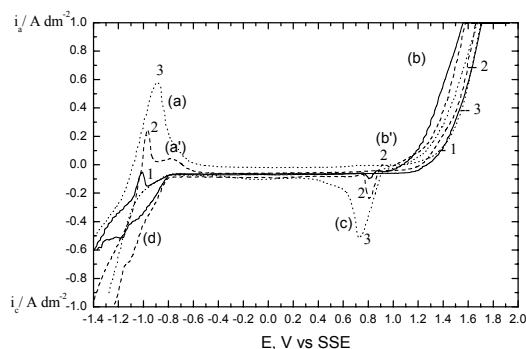


Fig. 3. CVA for a Pb-Co1.13%-Ti1.72%: 1 - 0 h polarization; 2 - 24 h polarization; 3 - 48 h polarization.

### Scanning electron microscopy

Figure 4 presents the morphological structure of the composite electrode Pb-Co1.22%-Ti2.48% before electroextraction. Asymmetrical crystal grains with clearly outlined boundaries between them have been observed. The surface is comparatively heterogeneous. Individual clusters can be detected, which is probably, due to the Co-Ti particles included.

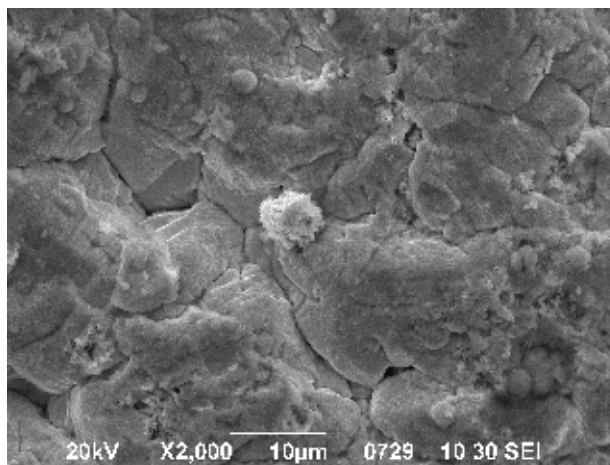


Fig. 4. Microstructure of composite electrode Pb-Co-1.22%-Ti-2.48%. Magnification 2000.

Figure 5 shows the morphological structure of the composite electrode Pb-Co1.22%-Ti2.48% after 72 hours of electroextraction. Typical pyramidal crystals of  $\text{PbSO}_4$  as well as needle-like ones of  $\beta\text{-PbO}_2$  have been observed. The granular clusters, detected at some places, are, most probably, due to the Co-compounds, which could, eventually, emerge as active centres on the surface. The latter may be considered as the reason for the depolarization effect of Co, leading to the decrease of the oxygen evolution overpotential.

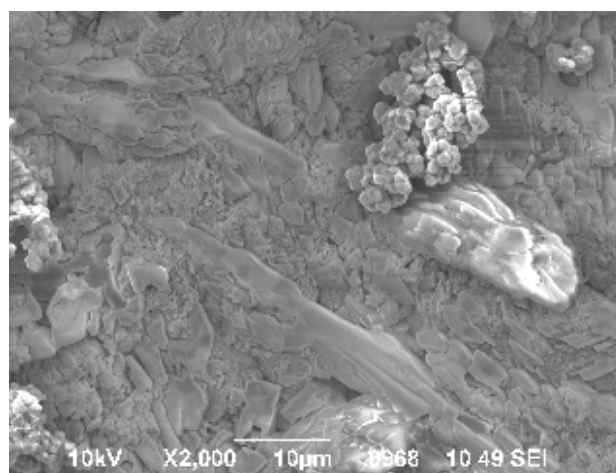


Fig. 5. Microstructure of composite electrode Pb-Co1.22%-Ti2.48% after 72 h of polarization. Magnification 2000.

## CONCLUSION

The composite anodes have exhibited a negligibly higher anode potential, compared with the cast Pb-Ag-1% alloy, in accordance with the galvanostatic polarization investigations. The corrosion resistance of the new anodic materials is very good, while slime-formation, when working with them, is of smaller amount, compared with that of the classical electrodes. The anode oxide film and the cyclic voltammetry curves of the composite anodes, respectively, are very close to those of the cast Pb-Ag1% electrode. The morphological structure of the lead-cobalt-titanium anodes differs from that of the cast electrode in the emergence of granular clusters, most probably, due to the Co-Ti nanoparticles included.

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## ИЗСЛЕДВАНЕ НА КОМПОЗИТНИ ПОКРИТИЯ, ПРЕДНАЗНАЧЕНИ ЗА АНОДИ ПРИ ЕЛЕКТРОЕКСТРАКЦИЯ НА ЦИНК ОТ СУЛФАТНИ ЕЛЕКТРОЛИТИ

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(Резюме)

Изследвани са нови анодни материали и олово-сребърни сплави, получени по различни начини, които се използват като аноди при електроекстракцията на цинк от сулфатни електролити. Новите анодни материали представляват композитни покрития, състоящи се от оловна матрица и кобалтово-титанатна фаза. Покритията са отложени върху валцовани оловно-калциеви подложки. Кобалтът и титанът са включени в оловната матрица под формата на наночастици от  $\text{CoTiO}_3$ . Посредством галваностатични поляризационни изследвания е изучено поведението на оловно-кобалтово-титанатните аноди по време на цинковата електроекстракция, а чрез циклична волтаперометрия са установени процесите, протичащи върху тяхната повърхност. Повърхностната морфология на композитните покрития е изследвана посредством сканираща електронна микроскопия.

Установено е, че анодният потенциал на изследваните композитни електроди е незначително по-висок от този на класическите оловно-сребърни сплави. Върху циклично-волтаперометричните криви, снети при използването на композитните електроди, са регистрирани същите характерни пикове, както и при използването на чист оловен анод.