

ELECTROCHEMICAL BEHAVIOUR OF LEAD-TITANIUM COMPOSITE ANODES DURING ZINC ELECTROWINNING

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ABSTRACT

A new anodic material for zinc electrowinning from sulphate electrolytes has been developed. This is a lead-titanium alloy coated lead composite electrode containing titanium nanoparticles. The behaviour of the lead-titanium anodes during the zinc electrowinning has been studied by means of galvanostatic polarisation investigations and cyclic voltammetry. The surface morphology of the composite lead-titanium electrodes was investigated by scanning electron microscopy.

Keywords: composite electrodes, zinc electrowinning, titanium, anodic polarization

INTRODUCTION

One of the most essential problems of the electrowinning of zinc from sulphate electrolytes is that of the insoluble anodes. The demands and requirements for purity and quality of the anode product are closely related to the creation of new anodic materials, possessing increased resistance in combination with other technological and electrochemical properties. This problem is being approached by trying to improve the electrocatalytic properties, attain a high corrosion resistance and improve the physicomechanical properties of the anodes. Research efforts have been directed towards substitution of the classical lead-silver anodes with other, less expensive anodic materials with improved parameters.

The literature describes numerous double, triple and even quadruple lead-based alloys as insoluble anodes but unfortunately very few of them have proved to be useful for any industrial application. These are first and foremost the alloys of lead with Sb, Ca, Ag, As, Cu, Te and Co[1]. With the exception of Ag and Co, which show certain electrocatalytic effects with respect to the reaction of oxygen evolution,

the rest of the listed alloy elements affect primarily the structure of Pb. Such an element is Ti. Regrettably the literature contains little data concerning its effect on anode behaviour.

Concerning the Pb-Ti alloys, the presence of the phase Ti_4Pb has been found [2] and it has been presumed that the formation of Ti_2Pb is possible. Obtaining such alloys is associated with certain difficulties and it has therefore become necessary to use some special methods of making alloys: fusing like arc welding through ultrasound and by means of scorching of composites. Including 1% Ti into Pb increases its anode resistance by 25-30%. At the same time the metallic-ceramic composition of the powders of Pb and Ti particles provide faster metal recovery than uncoated Pb. Addition of titanium salts to the solution does not affect the resistance of the Pb anode. It can therefore be assumed that Ti and its compounds do not take part in the process of oxygen evolution. That is why the increase of the resistance of the Pb-Ti anode as a function of structural factors must be considered.

It has been found [3] that lead-silver anodes, alloyed with other metals (such as Ti), besides other qualities, exhibit high corrosion resistance. On their industrial application, the warranty of the insoluble anodes increases and the consumption of silver decreases by 50%. These properties are determined by the concentration of the alloyed additives, which makes it possible to correct the technological characteristics of the anodic alloys during the electrolytic treatment of the zinc containing effluent.

The performance of titanium anodes coated with oxides of Ir-Co or Ir-Ti has been compared using long term polarization techniques under simulated electro-winning conditions [4]. Possible reasons for anode failure were explained using SEM and XRD data. Potentiodynamic studies in 2M H_2SO_4 indicated that a reduction of approximately 450 mV in the anodic potential can be achieved with Ti/(Ir-Co), compared to lead. This anode is also suitable in chloride contaminated sulphate electrolytes. The anodic potential measurements in different electro-winning electrolytes indicate that a potential saving up to 370–420 mV can be achieved. It is interesting to note that a mixed electrolyte, containing sulphate and chloride, behaves similarly to a pure chloride electrolyte with respect to the anodic potential.

This paper describes a new lead-titanium alloy coated lead-calcium composite anode for zinc electro-winning from sulphate electrolytes. Titanium is under the form of TiO_2 . The behaviour of these lead-titanium alloy composite anodes has been studied by galvanostatic polarization investigations.

EXPERIMENTAL DETAILS

Conditions for the preparation of the composite coatings

The new anodic materials are lead-titanium composite coatings, which are electrodeposited onto lead-calcium (Pb-0.08Ca) 20x20 mm plates. Their pre-processing included ultrasound degreasing in technical grade ethanol and electrochemical degreasing in a $NaOH + Na_3PO_4 \cdot 12H_2O$ solution, followed by chemical etching in HBF_4 . The composite coatings were electrodeposited in a lead

ammonium sulphamate electrolyte (LASE) that contained: 150 g dm^{-3} $\text{Pb}(\text{SO}_3\text{NH}_2)_2$, 100 g dm^{-3} $\text{NH}_4\text{SO}_3\text{NH}_2$, and 50 g dm^{-3} free HSO_3NH_2 . The LASE contained also 0.2 g dm^{-3} glue, as well as TiO_2 nanoparticles at a concentration of 5 g dm^{-3} . The electrodeposition was carried out at a constant temperature $T=25\pm 1^\circ\text{C}$, pH value of the electrolyte 1.3, volume 200 ml, cathodic current density $i_c=1 \text{ A dm}^{-2}$, magnetic stirring ($w=600 \text{ min}^{-1}$). The average thickness of the Pb-TiO₂ (lead-titanium) composite coatings was 60 μm . The counter electrodes were lead plates (99.97%) with a thickness of 5 mm.

Experimental methods

Full experimental details are supplied elsewhere [5-9]. Microprobe X-ray analysis was carried out using a JEOL 733 microscope. Galvanostatic polarization studies and cyclic voltammetry investigations were carried out using a galvanostat of type HTP30; 5 (Bulgaria) and a potentiostat of type ELPAN (Poland).

RESULTS AND DISCUSSION

Galvanostatic polarization investigations

Galvanostatic polarization investigations were employed to determine the anodic potential as a function of the time during the electrowinning of zinc from sulphate electrolytes. The anodes were Pb-Ti alloy coated lead-calcium with an effective area of 2 cm^2 . The cathodes were two aluminium plates with total working area equal to that of the anode. The reference electrode was mercurous sulphate (SSE) with a potential $E_{\text{SSE}}=+0.610 \text{ V}$ (NHE). A model electrolyte was used, containing 55 g dm^{-3} Zn^{2+} (as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), 180 g dm^{-3} H_2SO_4 and 5 g dm^{-3} Mn^{2+} (as $\text{MnSO}_4 \cdot \text{H}_2\text{O}$). During the electrowinning of zinc the temperature was kept constant at $37\pm 1^\circ\text{C}$. The alteration of the anodic potential as a function of deposition time of the Pb-Ti composite coatings is presented in Fig. 1. The anodes Pb-Ti-1.13% (curve 2) and Pb-Ti-0.46% (curve 3) show similar values of potential. The electrode containing a lower level of Ti again shows a more negative potential. As observed previously, the composite coatings exhibit a more positive potential than Pb-Ag-1%. After continuous polarization in the galvanostatic regime, the anodic films change; they become dark in colour, exhibit volume changes, become loose and easily crumble at the surface of the anode. Initially the electrolyte has a pink coloration but later becomes muddy brown due to the MnO_2 slime that is deposited on the walls and bottom of the cell. It is supposed that the depolarising effect on continued polarization is due to the larger active anodic area.

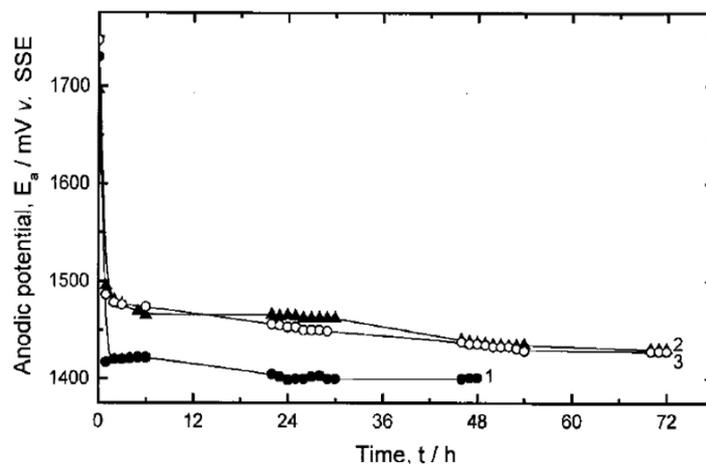


Figure 1. Dependence of the anodic potential on the time.
 1–Pb-Ag-1%; 2–Pb-Ti-1.13; 3–Pb-Ti-0.46%.

Cyclic voltammetry (CVA) investigations

The anodes used in the cyclic voltammetry investigations were those with a lower anodic potential. The electrode area was 1 cm^2 and the cathode, an aluminium plate of the same area. The reference electrode and the electrolyte were as described above. The experiments were carried out at room temperature. The potential was first scanned from -1.4 to 1.9 V at a sweep rate of 10 mV s^{-1} . The electrode was then polarized over 24 h at a current density of 5 A dm^{-2} . After the polarization, the cyclic voltammogram (CVA) was obtained. This was repeated once more. The CVAs of the Pb-Ti-0.46% electrode are shown in Fig. 2.

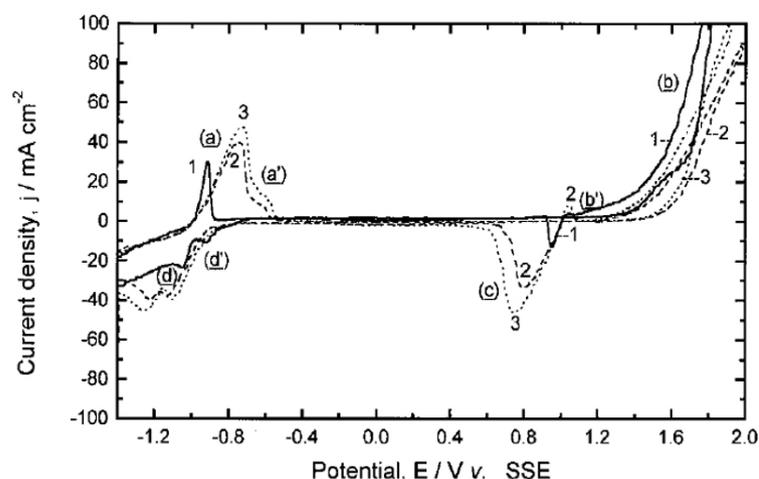


Figure 2. Cyclic voltammetry for a composite electrode Pb-Ti - 0.46%;
 Sweep rate= 10 mV s^{-1} . 1–0h anodic polarization; 2 – 24h anodic polarization; 3 – 48h
 anodic polarization.

All curves (curve 1 – 0 h polarization, curve 2 – 24 h polarization and curve 3 – 48 h polarization) exhibit four base peaks and one additional peak [10-12] determined by the following processes:

peak (**a**): $\text{Pb} \rightarrow \text{PbSO}_4$

peak (**b**): $\text{PbSO}_4 \rightarrow \text{PbO}_2$ and evolution of O_2

peak (**c**): $\text{PbO}_2 \rightarrow \text{PbSO}_4$

peak (**d**): $\text{PbSO}_4 \rightarrow \text{Pb}$

peak (**d'**): $\text{PbO} \rightarrow \text{Pb}$

Shifting of the lead sulphate peak **a** after polarization of the electrode (curves 2 and 3) in the direction of the passive zone is much more evident. A new anodic peak **a'** appears in curves 2 and 3 as a result of lead oxysulphate ($\text{PbO} \cdot \text{PbSO}_4$) formation [13]. Within the region of the second anodic peak, **b**, the curves are abruptly shifted in the positive direction after polarization of the electrode. In this case, the roughness of the surface as a result of the formation of loose PbO_2 layers is smaller. After 48 h polarization (curve 3), an opposite hysteresis of the CV is observed. The peak **b'**, caused by the oxidation of Pb to PbSO_4 through the PbO_2 pores appears only after 24 h polarization (curve 2). The reduction peaks **c** show a characteristic shifting in negative direction, corresponding to the shift of the anodic peak **b**. As expected, during polarization, the area of the reduction peaks **d** and **d'** increases and these peaks are shifted in the negative direction.

Electron microscopy investigations

Scanning electron micrographs (SEMs) of the lead-titanium composite coatings in Figs. 3 and 4 reflect the surface morphology of the coatings prior to the electrochemical investigations. The SEMs show that the crystal grains change from the pyramidal type to a more rounded and disordered structure. As mentioned in the galvanostatic polarization investigations, the electrodes with a Ti content of about 0.5 wt% were characterized with the lowest anodic potential of all the lead-titanium alloy coatings investigated. The surface morphology of the electrode Pb-Ti-0.46% after 72 h is shown in Fig. 4. Crystals of PbO_2 and prismatic crystals of PbSO_4 , as well as presence of Mn (the darks zone of the micrograph) under the form of the MnO_2 or Mn_3O_4 are observed.

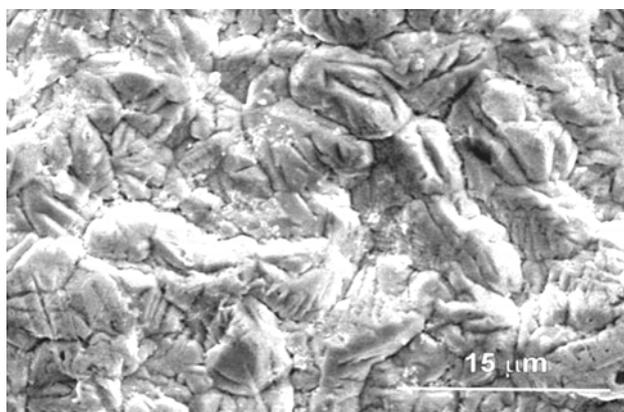


Figure 3. *Microstructure of composite electrode Pb-Ti-0.55%. Magnification x2000.*

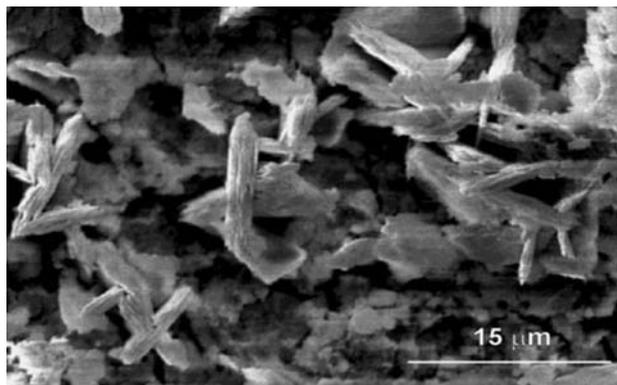


Figure 4. Microstructure of composite electrode Pb-Ti-0.46% after 72h electrowinning. Magnification x2000.

CONCLUSIONS

Composite Pb-Ti electrodes using TiO₂ nanoparticles have been obtained. It has been established that the optimal content of Ti in the composite coatings is about 0.5 wt%. It has been established that the anodic potentials of the investigated lead-titanium composite electrodes are similar but about 15mV higher than those of the classic lead-silver alloy Pb-Ag-1.0%. It has been shown by potentiodynamic cyclic voltammetry that the curves of the lead-titanium composite electrodes possessed the same characteristic anodic and cathodic peaks as those for a pure lead electrode. By electron microscopy investigations of the lead-titanium composite electrodes, orderly well formed pyramidal type crystal grains were shown. After the electrowinning process, the surface morphology of the lead-titanium composite electrodes displayed needle-type crystals of PbO₂ and prismatic crystals of PbSO₄, as well as the presence of Mn as MnO₂ or Mn₃O₄.

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