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Effect of pretreatment on the anodic behaviour of lead alloys for use in electrowinning operations. I

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Lead alloys are widely used as anodes in electrowinning operations, for the recovery of metals such as zinc, copper and chromium. When lead alloys are used as such it takes a long time for the build up of a compact, adherent and protective lead dioxide film. During the initial period prior to the build up of the compact layer of lead dioxide, the rate of anodic dissolution is very high, leading to a decrease in the purity of the cathode deposit. In order to minimize the duration of the conditioning of the anode, it is customary to build up a compact lead dioxide layer by pretreating the anodes in suitable electrolytes. An attempt is made to evaluate the performance of the pretreated electrodes by potentiodynamic methods.

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1. Introduction

In the electrowinning of zinc, copper and chromium, it is customary to use an alloy of high purity lead containing 0.1 to 2.5% silver as the anode material. The anode will be in the form of sheet. During the initial stages of the electrolysis, the reaction at the anode is the formation of lead dioxide. Once a compact lead dioxide film is built up, evolution of oxygen occurs. In the initial stages, the lead dioxide film is rather loosely attached to the anode surface and frequently falls to the bottom of the cell as anode mud. Part of the anode mud is suspended in the electrolyte as fine particles and gets incorporated in the cathodic deposit leading to a decrease in the purity of the metal deposit. Furthermore, the lead ions in the solution are deposited on the cathode. However, over a period of time, usually 3 to 6 months, the anode surface becomes stabilized with a hard, dense and adherent layer of lead dioxide and there is less carry-over of lead into the cathode deposit. The frequency of cleaning of the cell is also reduced. It has been reported [1] that additions of fluoride in low concentration up to 170 mg l^{-1} to the zinc sulphate electrolyte increases the corrosion resistance of the lead–silver alloy anodes.

Attempts were also made [2] to improve the quality of the lead dioxide formed in the initial stages of the electrolysis, by a step known as 'preconditioning' of the anodes so that a compact adherent layer was built up within a short time, which would reduce the corrosion of the anode during actual use. This 'preconditioning' involves treatment of the lead–silver alloy anodes, prior to use in electrolytic cell, in a fluoride or fluoride/sulphate solution. It has been reported that the anodes preconditioned in a fluoride solution ranging from 20 to 60 g l^{-1} fluoride at an anode current density of 3.7 to 5.1 A m^{-2} give a better performance in the electrolytic cell. The efficiency of the 'preconditioning' method is generally determined by observing the lead pick-up in the cathode deposit.

The object of the present investigation is to establish the optimum conditions of 'preconditioning' the electrodes to obtain a compact and adherent oxide coating on the surface which will minimize the initial dissolution of the lead alloy and consequent formation of anode mud. It is also proposed to examine whether the potentiodynamic method can be used as a rapid tool for the evaluation of such electrodes instead of adopting the time-consuming method of measuring the lead pick-up at the cathode.

2. Experimental

Lead–silver (1%) alloy electrode, cast in the form of rod of 4 mm diameter and embedded in a

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Teflon rod so as to give a surface area of 1 cm^2, was used. Before each experiment, the electrode was cathodically cleaned in sulphuric acid, washed with water and then with acetone. An H-type glass cell was used.

The anodic polarization was carried out by scanning the potential of the electrode at a rate of 9 mV s^{-1} using a mechanical ramp and Wenking potentiostat. The scan was started from the rest potential of the system. The currents were recorded as a potential drop across standard resistances. A saturated calomel electrode was used as the reference electrode and platinum and copper-coated platinum (in the case of zinc sulphate) were used as auxiliary electrodes.

A.R. grade chemicals were used. The measurements were carried out at room temperature (28 ± 1° C).

All the experiments were carried out at least three times. Although the passivation potential, potential range of passivation and potential of oxygen evolution were fairly reproducible (± 20 mV), the critical current for passivation and passivation current were reproducible only within a range of ± 20%.

3. Results and discussions

The anodic polarization curve as obtained by the potentiodynamic method is given in Fig. 1 for different concentrations of sodium fluoride. In all concentrations of fluoride studied here, the lead–silver alloy exhibits an active–passive behaviour with a fairly wide potential range of passivation. The passivation potential, E_p, varies with fluoride concentration and becomes more positive with a decrease in concentration of fluoride. However, the critical current for passivation, i_c, and passivation current, i_p, decrease with decrease in concentration of fluoride. These facts indicate that fluoride ion is involved in the formation of the passive film on the surface. At high fluoride concentration, the rapid dissolution of lead alloy leads to supersaturation and precipitation even at lower potentials. However, the film seems to be porous and less protective as indicated by the high values of i_c and i_p at higher fluoride concentrations. At lower concentrations of fluoride, though the passivity is established at more positive potentials, more compact films are formed, as is indicated from i_p and i_c. The high porous nature of

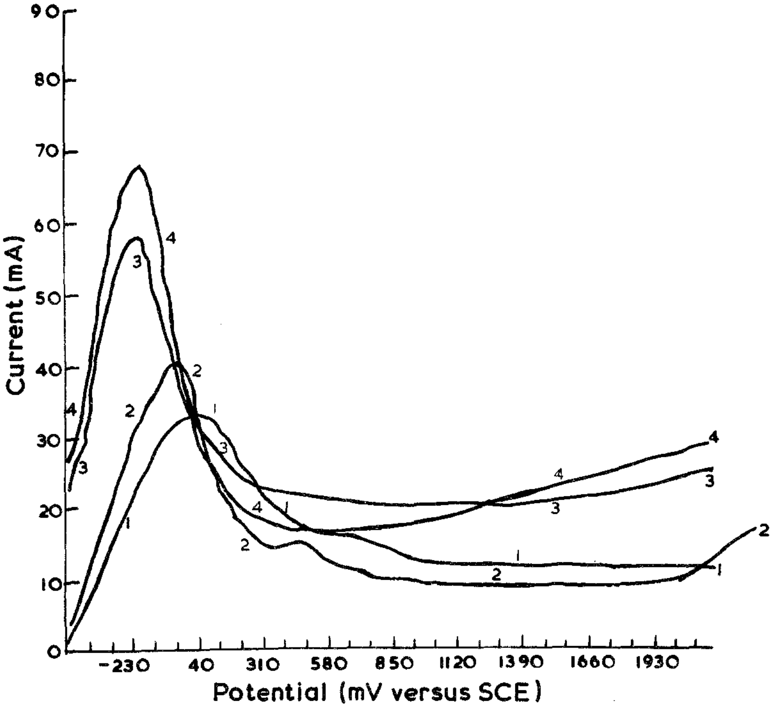

Fig. 1. Potentiodynamic anodic polarization curves for Pb–Ag (1%) alloy electrodes in sodium fluoride solutions 1, 5 g l^{-1}, 2, 10 g l^{-1}, 3, 20 g l^{-1}, and 4, 30 g l^{-1} fluoride solution.

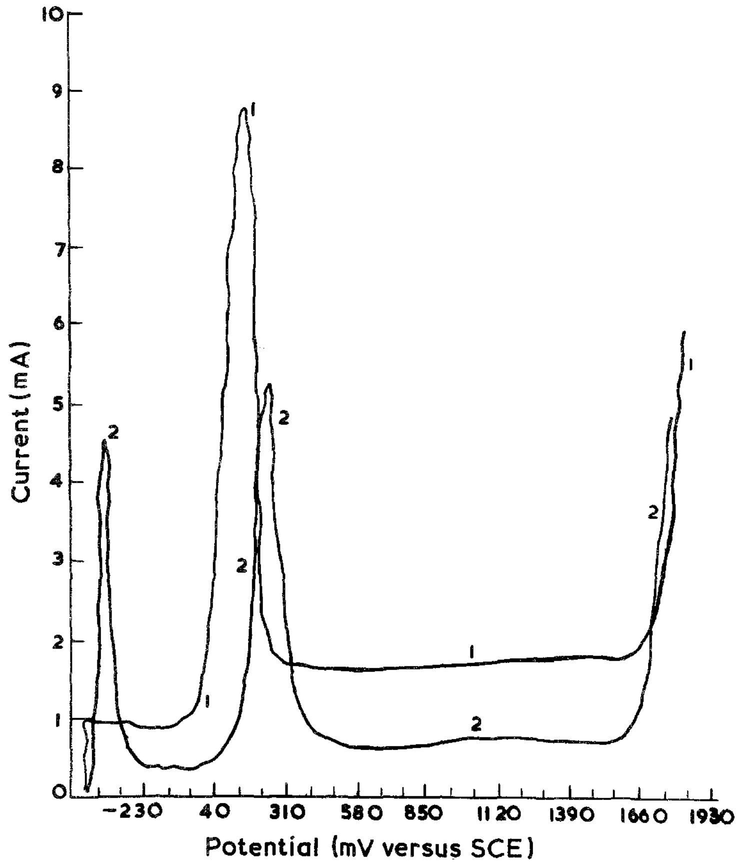

Fig. 2. Potentiodynamic anodic polarization curves for Pb–Ag (1%) alloy electrodes in sulphate solutions. 1, In zinc sulphate solution. 2, In sodium sulphate solution.

the film formed at high fluoride concentrations is also reflected in the performance of the 'preconditioned' electrodes in zinc sulphate solution as will be seen later (Fig. 3).

The electrodes passivated in fluoride solution (Fig. 1) exhibit a wide potential range of passivation from + 300 mV to 2.2 V (versus saturated calomel electrode) and the oxygen overpotential is substantially increased. This aspect assumes significance when one compares the passivation behaviour of lead–silver alloy in fluoride solutions with that in sodium sulphate/zinc sulphate solutions. Fig. 2 shows the anodic behaviour of the lead alloy in sodium sulphate and zinc sulphate solutions where the sulphate concentrations correspond to the conditions of electrowinning operations. In sulphate solution, two distinct passivation regions are obtained which may correspond to the formation of lead sulphate and/or lead monoxide and lead dioxide. The two waves are not clear in the fluoride solutions under the present conditions. It may be observed that compared to fluoride solutions, the critical current (i_c) and the passivation current (i_p) are much lower in sulphate solutions, although the second and effective passivation potential is even more noble than that corresponding to the lowest fluoride concentration. However, the transitions are very sharp in sulphate solution.

The potential region of passivation is comparatively narrow (+ 300 mV to 1.6 to 1.65 V) in the case of sulphate solutions, and oxygen evolution also starts at lower potentials.

The behaviour of the electrodes 'preconditioned' by the anodic scan from – 500 mV to oxygen evolution potential in different electrolytes has been compared by polarizing them anodically in zinc sulphate solutions of concentrations used in electrowinning operations. The results of this study are shown in Fig. 3. The anodic currents obtained in the case of electrodes 'preconditioned' in sulphate solution are much

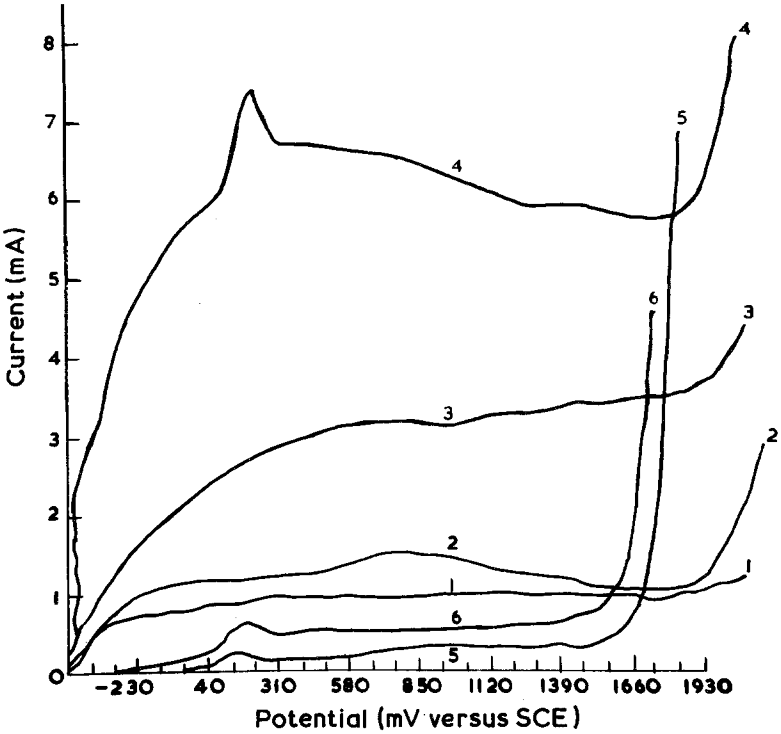

Fig. 3. Potentiodynamic anodic polarization curves for preconditioned Pb–Ag (1%) alloy electrodes in zinc sulphate medium. Preconditioned in 1, 5 g l^{-1}, 2, 10 g l^{-1}, 3, 20 g l^{-1}, 4, 30 g l fluoride solution, 5, zinc sulphate solution and 6, sodium sulphate solution.

lower than those obtained during the 'preconditioning' operation indicating that the film formation has been effective. The currents obtained in the case of electrodes 'preconditioned' in fluoride solutions are much larger, the largest value being obtained from the electrode treated in the highest fluoride concentration. It is interesting to note that the potential of oxygen evolution of these electrodes has a tendency to become less positive with increase in fluoride concentration and the electrode treated in 30 g l^{-1} fluoride has almost the same oxygen overpotential as the electrode treated in sulphate solution.

These results would compel one to conclude that the electrode 'preconditioned' in sulphate solutions should behave much better than those 'preconditioned' in fluoride solutions. However, it has been fairly well established that the fluoride-treated electrodes lead to lower anodic dissolution. This, at present, is difficult to understand. Another important fact to be noted is that although the passivation currents are larger for fluoride-treated electrodes, the oxygen overpotential is enhanced by nearly 450 mV. It is possible that the structure and compactness of the film formed under these conditions is different.

More detailed studies designed to understand the characteristics of the film formed under different conditions, to evaluate the protective characteristics of the films formed under steady state conditions and also to establish the optimum conditions of treatment of the electrodes are in progress.

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