

PLATINUM PLATED TITANIUM FOR INDUSTRIAL ELECTROLYSES

MALATHY PUSHPAVANAM AND S R NATARAJAN

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

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The utilisation of Pt-Ti anodes in industrial electrolytic processes, such as electroplating, electrochemical production and sewage treatment are well known. Such electrodes prepared at CECRI have been found to be useful also in electrochemical processing of nuclear wastes under highly corrosive conditions.

The performance of platinum plated titanium in sulphuric acid and sodium chlorate solution has been evaluated using potentiostatic polarization technique with supporting data on their useful life. A comparison of the electrode behaviour with different thicknesses of platinum is also included.

Key words: Platinum plated titanium, electroplating, potentiostatic polarisation

INTRODUCTION

The ability of platinum to maintain titanium in the passive state, even though it may cease to be passive if uncoupled, has been known for many years [1-5]. Though titanium can be protected by coupling to many of the noble metals, the use of platinised titanium, justified on grounds of cost and reliability, has become particularly pre-eminent. Since 1957, it has been used widely all over the world in electroplating of nickel, copper, chromium and gold and also in various electrochemical processes as in electrolysis of sewage treatment and cyanide oxidation.

In electrolytic cells, if the anodes used are not completely inert, they will be slowly consumed leading to contamination of the electrolytes and need to be replaced periodically. Inertness may involve passivity, but if a cell is to be operated with a high current, either anodes of large areas have to be employed or a secondary anode reaction such as oxygen evolution has to be allowed without affecting the anode surface deleteriously. In this respect, the virtues of platinum or a platinum electroplate as an anode are that the substrate is protected and a higher overpotential for oxygen evolution than with other metals enables operation at a lower cell voltage.

An elegant process worked out at the Central Electrochemical Research Institute provides a porefree, adherent platinum coating on titanium, a substrate which does not easily permit any metal to be plated upon it with adequate adhesion due to the presence of a tenacious, passive oxide film on the surface [6]. Using the new process, adherent platinum deposits can be produced on titanium even upto thicknesses of 8-10 μm . For electrochemical processing, a coating of 2-3 μm is generally used [7].

The investigation forming the subject of this paper was undertaken to examine the performance of platinum-plated titanium anode (produced at CECRI), in sulphuric acid and chlorate media of which the former is used widely in industrial electrochemical processes [7] and electroplating, and the latter for production of perchlorates [8].

EXPERIMENTAL

Platinum plating on titanium was carried out from the electrolyte based on dinitrosulphato-platinous acid [9, 10] prepared using pure platinum foil as the raw material. Deposits of different thicknesses from 0.25 to 3.0 μm were produced. The porosity of the deposit was assessed by heating the specimens in air upto about 873K

and examining the coloured spots of titanium oxide formed at the exposed areas [6].

The behaviour of plated anodes was investigated by the potentiostatic polarisation technique. A potentiostat (Wenking Model LB 75L) connected to a scan generator (Wenking Model VSG 72) and a XY-t recorder was used for the measurements.

The potential was scanned at various levels at a rate of 2 mV.s^{-1} . A conventional H-type cell was used in which the anode samples were held centrally, with a platinum auxiliary electrode in a separate compartment. The potential was monitored by means of a saturated calomel electrode (SCE).

Commercially pure titanium (Tikutan) specimens of $1 \times 2 \text{ cm}$ size were chemically etched in a special etching solution containing hydrochloric acid [11]. Anodic polarisation was carried out using platinum, titanium and platinum-titanium bi-electrode [12] having area ratios of 1:1, 0.5:1, 0.25:1, 0.04:1 and 0.02:1.

The effective life of the Pt-Ti electrodes with different coating thicknesses was assessed from the duration required to acquire the breakdown potential [13] at a constant current density of 500 mA.cm^{-2} in a separate cell having a cathode of 20 cm^2 area. Potentials with reference to SCE were recorded at one hour intervals.

Analytical grade sulphuric acid and double recrystallised sodium chlorate were used for preparing solutions of 1.0M and 6.0M concentrations and were pre-electrolysed suitably before use.

RESULTS AND DISCUSSION

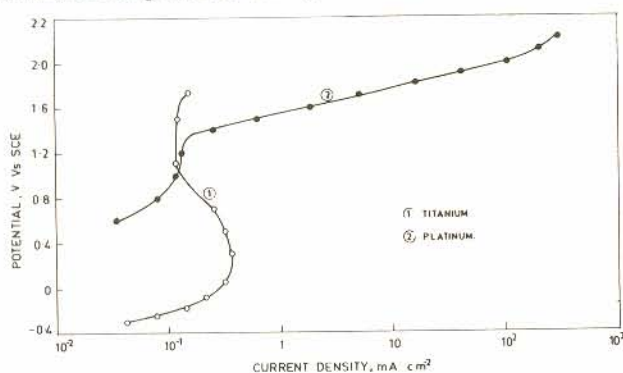
Slow dissolution of titanium substrate through pores in the platinum coating can lead to detachment of the coating and subsequent loss of coating activity. Hence, production of coatings with a very low porosity is a prerequisite for minimising, substrate attack and reduction of anode polarisation especially under highly acidic conditions. From the results of porosity (Table I), it is evident that coatings of more than 0.75 μm thickness are porefree. This test is also indicative of the good bonding between substrate and the coating, as otherwise the coating will peel off because of the differences in the thermal expansions of the coating and the substrate.

The deleterious role of pits in the coating can be understood from the polarisation studies involving Pt-Ti bi-electrodes with varying platinum area. Figure 1 shows the anodic behaviour of titanium and platinum in sulphuric acid medium. Titanium

TABLE-I: Porosity of platinum deposits

No.	Deposit thickness (μm)	Porosity as % defective area	Nature of coating
1	0.25	25%	Grey matt
2	0.50	5%	White matt
3	0.75	Nil	White semibright
4	1.00	Nil	White bright
5	3.00	Nil	White bright

acquires passivity at a very low current density whereas platinum shows increasing current density even above 2.0V.

Fig. 1: Anodic behaviour of titanium and platinum in 1.0M H_2SO_4

Coupling platinum to titanium represents a practically convenient arrangement to understand the effect of porosity in platinum deposits, on the anodic behaviour of Pt-Ti anodes. The low areas of platinum have the most valuable effect on the passive nature of the bi-electrode. Figure 2 shows the polarisation curves of the bi-electrodes of different area ratios. As the platinum area increases, the passivation current density increases and the bi-electrode becomes more and more active. With an area ratio of 2:1, practically the passive region is found to vanish. However, the Pt-Ti electrodes under test (Fig. 3) show no signs of passivation indicating that the thickness of platinum chosen (even at 0.25 μm thickness) represents an area of above 2:1. However with an increasing coating thickness upto 0.75 μm , there is a gradual decrease in overpotential which can be attributed to the increased catalytic activity of the electrodes. Still higher platinum thicknesses do not register appreciable change in the overpotential.

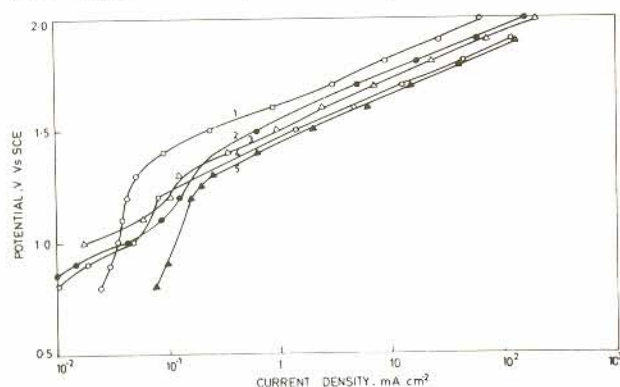


Fig. 2: Anodic behaviour of Pt-Ti bielectrodes of different area ratios in 1.0M H_2SO_4
(1) 0.025:1 (2) 0.04:1 (3) 4:1 (4) 2:1 (5) 1:1

In practice, slow dissolution of titanium substrate via pores in platinum deposits leading to their detachment and subsequent loss

of activity, is a process often requiring several months of operation to become apparent. The effective life study of electrodes having varying platinum thicknesses, as given in Table II can, however, be an indicator of the trend. Coatings with 0.25 or 0.5 μm thickness fail at a fairly earlier stage than those having a thickness well above 0.75 μm . However on considerations of the slow dissolution of platinum [7], the advantages of extending the life of the electrode and the necessity of producing porefree coatings, a thickness of 2.0 μm can be recommended for industrial applications.

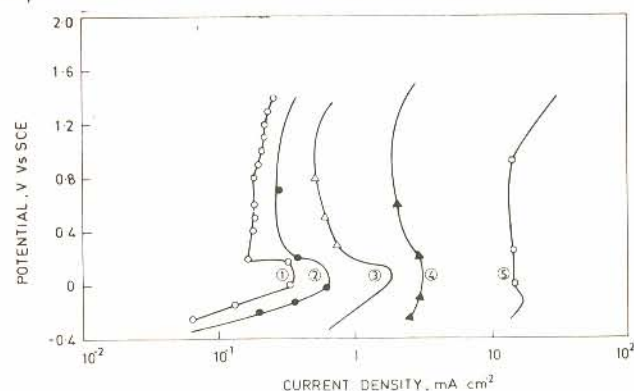


Fig. 3: Anodic polarisation of Pt-Ti electrodes with different coating thicknesses in 0.1M H_2SO_4
(1) 0.25 μm (2) 0.50 μm (3) 0.75 μm (4) 1.00 μm (5) 3.0 μm

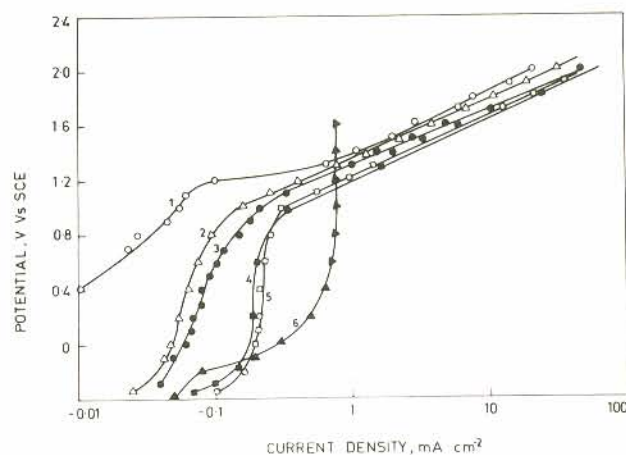


Fig. 4: Anodic behaviour of platinum, titanium and Pt-Ti electrodes in 6.0 M sodium chlorate solutions

TABLE-II: Results of effective life study

No.	Deposit thickness (μm)	Time elapsed before assumption of breakdown potential (h)
1	0.25	10.5
2	0.50	50.2
3	0.75	Not failed even after 300
4	1.00	" " "
5	3.00	" " "

A similar behaviour has been observed in sodium chlorate solution where the anodic reactions include formation of perchlorate. Under a mildly acidic condition of the anolyte, the overpotential of the anodic reaction is higher than that observed for sulphuric acid (Fig. 4). But the effect of the thickness of coating on the polarisation characteristics generally remains the same. A slight

increase in current density for the Pt-Ti electrodes (especially with more coating) in both the media, may be attributed to the increased surface area of the electrodes due to the etching treatment.

CONCLUSION

Platinum-plated titanium produced using the CECRI process in which the platinum coating is not less than 2 μm thickness can function effectively in sulphuric acid and chlorate media.

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