Diffusion Alloyed Platinum Electroplated Titanium Electrodes for Electrochemical Processes

EXECUTIVE SUMMARY

In the acid killing by electro-reduction process, concentration of nitric acid in the high level waste (HLW) from the spent nuclear fuel reprocessing plant has to be brought down from about 4 to 0.5 M in order to reduce the amount of HLW by subsequent evaporation and to minimise the corrosion in waste tanks during storage of the concentrated waste solution. For this purpose, electrodes with high performance and corrosion resistance are demanded. Platinum electroplated titanium (PET) has been selected as electrodes for this purpose, however, plated surfaces have numerous defects affecting the integrity of the electrodes during service. Pt electroplated Ti (PET) and diffusion alloyed PET (DAPET) of plating thickness 3, 5, 7 and 10 µm was evaluated for their performance. The electrochemical reduction of 4 and 8M nitric acid to near neutral conditions was carried out with the above-said anodes and Ti cathode at various cathodic current densities. The PET and DAPET electrodes could withstand and function well at much higher cathodic current densities (up to 80mAcm−2). It is recommended that for plant applications at high current density and acidity, Pt electroplated to a thickness of above 7 µm over Ti substrate followed by diffusion alloying may be employed to make a compromise between the energy efficiency of the process and the life extension of the anode.

OUTLINE

Platinum finds extensive application as electrode materials in chemical and electrochemical industries due to its high conductivity, good electrocatalytic activity, and excellent resistance to oxidation and corrosion. However, owing to its high cost in bulk form, platinum is put to practical use by electroplating a thin layer over high corrosion resistant substrates such as titanium, niobium and tantalum. Platinum electroplated Titanium (PET) electrodes have become an inevitable component in electrochemical industries, and in particular to electrochemical processes wherein high corrosive and radiation fields are envisaged. One such application is the use of PET electrodes in the spent nuclear fuel reprocessing plants.

One of the mechanisms involved in the failure of the electroplated anodes during continuous use is by delamination of Pt from the surface. When delamination occurs in PET electrodes, the plated Pt gets detached from the surface and titanium metal would be exposed to the electrolyte resulting in the failure of the electrode. In addition, the plated surface, depending on the thickness, would develop a number of defects (Fig. 1) like micropits, microcracks, etc. The micro cracks were formed during the stress relieving process (to remove the residual stresses produced in the material during the plating process). Ti substrate attracts Pt from the bath solution in all directions and there would be some discontinuity in the Pt layer on the Ti surface, which were observed as pits or islands. The pit is not bare Ti but a layer of Pt with lower thickness. With increased thickness of plating, the micro cracks formed were more pronounced and when the thickness exceeded the limiting value, peeling off of Pt would occur. As the thickness of plating increases, the formation and propagation of cracks also increase owing to stress relieving process. At locations where the micro cracks meet each other, they form junctions such as triple points in which the most wide and deep opening would be present on the surface as is evident

Platinum electroplated titanium is subjected to a heat treatment in vacuum well above the hcp (α) to bcc (β) structure transition temperature of Ti for sufficiently longer durations, inter diffusion of Pt (deposited over the surface of Ti) occurs in the bcc lattice of Ti, as this high temperature phase is a open structure with more void space. This treatment produces intermetallic Pt–Ti compounds on the surface and delays the process of delamination of elemental Pt and thus extends the life of the electrode. During diffusion annealing of PET anodes, an inter-diffused layer is formed between Ti surface and plated Pt (Fig. 2).

Therefore, industries using plated electrodes for continuous operation at high current density conditions in corrosive environment should exploit this diffusion annealing procedure to extend the life of the electrodes.

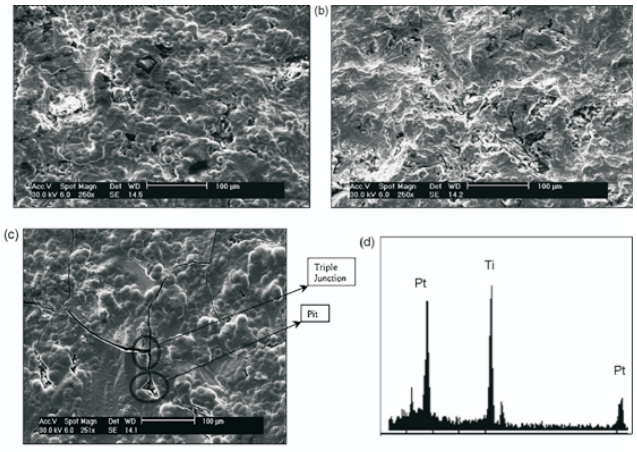

Fig. 1 : SEM micrographs showing platinum electroplated surface of titanium showing various defects

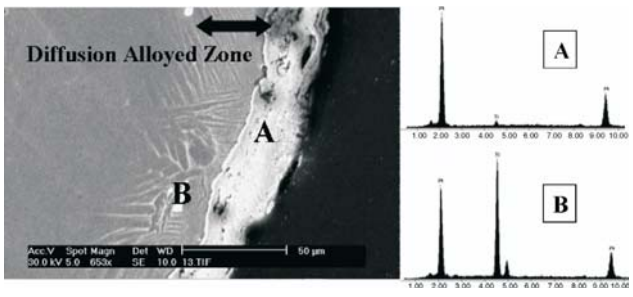

Fig. 2 : SEM micrograph of diffusion annealed PET sample showing the presence of Pt in the inter diffused zone 'B' within the Ti substrate

■ ADDITIONAL INFORMATION

Platinum electroplated titanium electrodes are candidate materials for applications in electrochemical processes employed in reprocessing plants. One of the draw back of the electrode is the defects present on the plated surface which allows an easy path for the penetration of electrolyte leading to corrosion of titanium and failure of the electrode. To overcome this difficulty, a novel diffusion alloying process has been evolved by which an inter-diffused layer enriched with PtTi intermetallics is developed. Thus the penetration of corrosive electrolyte would meet the diffusion alloyed intermetallic zone, and hence the corrosion attack and failure of electrode would be avoided.

■ GENERAL EXPLANATION RELATED TO THE DESCRIPTION

One of the mechanisms involved in the failure of the platinum electroplated titanium electrodes during continuous use is by delamination from the surface. When delamination occurs in PET electrodes, the plated Pt gets detached from the surface and titanium metal is exposed to the electrolyte resulting in the failure of the electrode. During diffusion alloying of PET anodes, an interdiffused layer is formed between Ti surface and plated Pt. The interdiffused layer comprises the intermetallic compounds $PtTi_3$ and PtTi. When delamination occurs, the DAPET electrode is not susceptible to sudden failure due to the adherent Pt-Ti interdiffused layer which protects the surface of Ti substrate. The electrodes were employed in the electrolytic destruction of nitric acid from 4 or 8 M to near neutral conditions. The rate of destruction of the acid and the rate constant were computed from the experimental results using kinetic equations. A comparison was made on the current efficiency of the process with respect to plating thickness and current densities to facilitate the performance evaluation of the electrodes, and the electrodes are seen to be performing at comparatively lower efficiency levels (Table 1). Therefore, industries using Pt plated Ti electrodes for continuous operation at high current density conditions in corrosive environments are recommended to use diffusion alloyed electrodes.

Table 1
Comparison of the performance of the anodes, PET and DAPET in terms of energy efficiency of the electrolytic process

S. No.	Anode	Rate of reduction ($mol.A^{-1}.h^{-1}$)	Rate constant ($mol.L^{-1}.h^{-1}$)	Current efficiency (%)
1	3-PET	0.0167	1.781	67.2
2	5-PET	0.0179	1.911	73.9
3	7-PET	0.0197	2.103	79.4
4	10-PET	0.0196	2.089	78.8
5	3-DAPET	0.0183	1.964	73.6
6	5-DAPET	0.0189	2.016	76.0
7	7-DAPET	0.0194	2.080	77.9
8	10-DAPET	0.0197	2.096	79.0

■ BRIEF DESCRIPTION OF THEORETICAL BACKGROUND

The Ti base metal undergoes a solid state phase transformation from hcp (α) to bcc (β) structure at about 1163 K. When platinum electroplated titanium is subjected to a heat treatment in vacuum well above the transition temperature of Ti for sufficiently longer durations, inter diffusion of Pt (deposited over the surface of Ti) occurs in the bcc lattice of Ti, as this high temperature phase is an open structure with more void space. This treatment produces intermetallic Pt-Ti compounds on the surface and delays the process of delamination of elemental Pt and thus extends the life of the electrode.

■ ACHIEVEMENT

Platinum plated titanium electrodes consists of inherent defects generated during electroplating process which hinder the performance and service life. Diffusion alloying process has been established to develop an inter-diffusion zone consisting of inter-metallic phases of Pt-Ti, which improved the corrosion resistance and performance during electrolytic acid killing experiments.

■ PUBLICATIONS ARISING OUT OF THIS STUDY AND RELATED WORK

C. Mallika, B. Keerthika and U. Kamachi Mudali, *Electrochimica Acta*, **52** (2007) 6656.

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