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Electroless deposition of platinum on titanium substrates

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Abstract

The use of an electroless platinum bath based on chloroplatinic acid and hydrazine for depositing adherent and uniform layers on titanium panels is demonstrated. The conditions were optimised for a new set of additives. The effect of concentrations of platinum metal in the bath on thickness of the deposit was studied. The deposition rates on titanium and gold-plated titanium are evaluated. Dispersed platinum coatings on titanium powder were successfully obtained. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electroless deposition; Synergistic effect; Stress-free deposit; Surface tension; Stabiliser

1. Introduction

Platinum is extensively plated onto aviation components, turbine blades, electrodes, electronic components and jewellery to improve corrosion properties or appearance. Platinum is a desirable electrode material for numerous potentially important industrial processes. However, the cost of this metal is prohibitive for use in many applications. In order to save this costly metal, it is desirable to use it in a highly dispersed form on various conductive supports like carbon, graphite, titanium, etc. These dispersed electrodes are useful in electroreduction of oxygen, electrocatalytic oxidation of methanol, etc., in fuel cells and metal–air batteries [1]. Platinum-plated titanium, neobium and Pt–Ru alloy-coated titanium have been employed in various electrochemical processes.

The electroless deposition of metals has attracted a great deal of interest as an economic means of metallisation of polymers. This technique has been shown to have significant potential for the fabrication of a new generation of electrodes used in implantable medical applications, such as defibrillation, pacing and cardiomyoplasty [2]. There are very few reports available in literature on the process of electroless deposition of platinum compared to any other noble metal. This may be due to the difficulties encountered in controlling the deposition of platinum by electroless technique from aqueous solutions, compared to the ease with which baths of palladium, gold, etc. are controlled. Noteworthy patents/papers describing the electroless platinum deposition were by Oster et al [3] using platinum sulphate and metal borohydride, Rhoda et al [4] using complex alkaline Pt(IV) hydroxide solution with hydrazine salts, and Leaman et al [5] using acidic and alkaline baths of chloroplatinic acid with hydrazine. The acidic bath contained sulphosalicylic acid as a stabiliser, 2,7-naphthalenedisulphonic acid disodium salt, and benzene sulphonic acid as other additives. The acidic bath electroless process was limited to depositing platinum layers over gold, palladium and ABS plastics [6].

Keeping the foregoing in mind, we describe the electroless platinum deposition from the acidic bath with improved additives containing more sulphonic acid functionalities to plate on titanium, gold-plated titanium panels and titanium powder. In this article, the results are presented and discussed.

2. Experimental

Chloroplatinic acid was purchased from Arora–Mathey. All other chemicals are of analytical grade.

The electroless bath solutions are prepared according to reported procedure with a few modifications [6]. A stock solution of chloroplatinic acid was prepared by dissolving 2 g in 100 ml of 4% HCl. An aliquot of 25 ml of $1\,g\,l^{-1}$ platinum bath was prepared by taking 3.2 ml of the stock solution and diluting to 25 ml with water. Required amounts of 1,3,6-naphthalene-trisulphonic acid trisodium salt ($0.1\,g\,l^{-1}$), benzene-*m*-disulphonic acid ($0.4\,g\,l^{-1}$) and sulphosalicylic acid ($1\,g\,l^{-1}$) were added to the bath. Solid hydrazine (as hydrochloride) was added ($3.7\,g\,l^{-1}$) to the bath just before the experiment is commenced. The deposition was carried out at 66–68°C using a thermostat.

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Titanium panels (1 cm × 5 cm) were sand blasted, and etched in concentrated HCl–HF solutions. Deposition was carried out on $1\,\mathrm{cm}^2$ area of the panel. The thickness of the deposits was measured by the XRF method using coating measurement instruments [CMI] type XRX-Xyz. The measurements are accurate up to ±0.1 mg and ±0.001 μm.

3. Results and discussion

3.1. The influence of additives

The electroless plating bath containing $1\,\mathrm{g\,l^{-1}}$ (of platinum metal), provide a process for the application of adherent layers of platinum on titanium metal, titanium powder and gold plated titanium panels. Base metals like copper, that are attacked by the acidic solutions of the bath, cannot be directly plated, without a suitable undercoat. The bath is stable without the addition of a reducing agent. The reducing agent is added prior to deposition. The efficiency of the bath is lowered if the deposition is interrupted and the system is cooled to room temperature. However, the bath can be reused with the addition of some more quantities of hydrazine. It is given in the literature that the addition of various salts of sulphonic acids improve the stability of the bath, reduction of stresses in deposits and lower the surface tensions of the bath [6]. The use of benzene sulphonic acid, 2,7-naphthalene disulphonic acid disodium salt as additives and sulphosalicylic acid as stabiliser was already investigated [6]. These additives were effective in lowering the surface tension of the bath and provided stress-free deposits. To explore the utility of additives containing more sulphonic acid functionalities, namely, benzene-*m*-disulphonic acid, and 1,3,6-napthalene-trisulphonic acid trisodium salt were added to the bath separately and the resulting stability of the bath, rate of deposition and deposit properties were studied.

The salt of 1,3,6-naphthalene trisulphonic acid was added, in quantities of $0.1\,\mathrm{g\,l^{-1}}$, to the bath and the resulting deposits on titanium panels examined. The coatings were black and adherent. When the amount is increased to more than $0.2\,\mathrm{g\,l^{-1}}$, the bath decomposed within 1 h. Similarly, the optimum concentration of benzene-*m*-disulphonic acid is found to be $0.4\,\mathrm{g\,l^{-1}}$. The deposits are gray-black and adherent. The use of higher concentration of this additive ($>0.4\,\mathrm{g\,l^{-1}}$) led to decomposition of the bath. When sulphosalicylic acid is used as an additive, the stability of the bath increased with increased brightness of the deposits. The effect of concentration of sulphosalicylic acid on the weight of the platinum deposit is shown in Fig. 1. It can be concluded that sulphosalicylic acid in a concentration of $1\,\mathrm{g\,l^{-1}}$ is optimum.

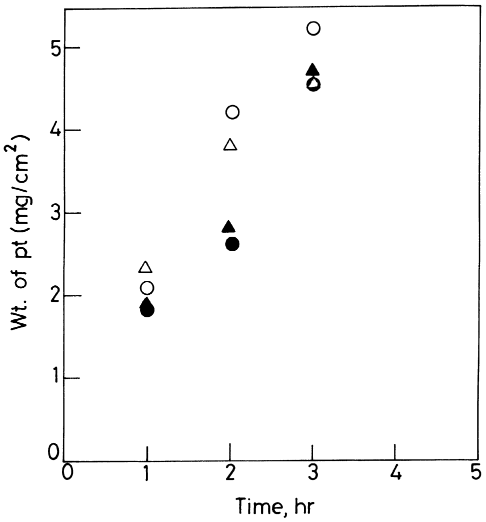

Fig. 1. The effect of sulphosalicyclic acid of (●) 0.2, (▲) 0.4, (○) 1, (△) $1.5\,\mathrm{g\,l^{-1}}$ on the weight of the platinum deposition with time.

The combination of the above three additives with their respective optimised concentrations in the bath were checked for the stability and appearance of the deposit. Fig. 2 represents the synergistic effect of the three additives on the stability and rate of deposition of the bath. The addition of three additives to the bath increases the efficiency and stability. It was observed that the deposits are gray-white and adherent. As the concentration of the sulphosalicylic acid is increased in the bath to $>1\,\mathrm{g\,l^{-1}}$, while keeping the other two additives concentration constant, the brightness of the deposit decreases. The panel plated for a 4-h duration is much less brighter than that plated for 1 h in a bath containing $1.5\,\mathrm{g\,l^{-1}}$ sulphosalicylic acid. It is also observed that although the life of the bath increased by 1 h, the efficiency was found to decrease. Thus, a bath containing $1.5\,\mathrm{g\,l^{-1}}$ of sulphosalicylic acid (Fig. 2), though stable for 4 h, the amount of platinum deposited in 4 h. is equivalent to that produced from a bath containing $1\,\mathrm{g\,l^{-1}}$ of the additive in 3 h. Thus, the bath

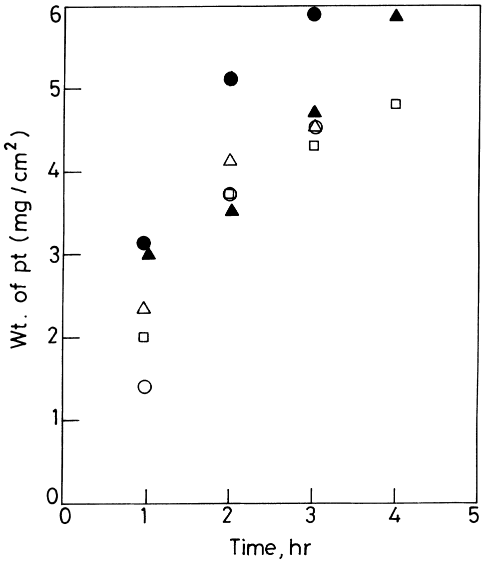

Fig. 2. Combined effect of the three additives: (i) 1,3,6 naphthaline trisulphonic acid trisodium ($0.1\,\mathrm{g\,l^{-1}}$); (ii) benzene-*m*-disulphonic acid ($0.4\,\mathrm{g\,l^{-1}}$); and (iii) sulphosalicyclic acid of (○) 0.2, (△) 0.4, (●) 1, (▲) 1.5, and (□) $2\,\mathrm{g\,l^{-1}}$.

with platinum concentration of $1\,g\,l^{-1}$ is optimised with the above additives concentrations.

3.2. Effect of platinum metal concentration in the bath

The effect of platinum metal concentration in the bath on the thickness of the deposit was examined. For this purpose, baths with 1, 2 and $3\,g\,l^{-1}$ of platinum concentrations were prepared. Platinum was deposited on titanium panels of 1-cm^2 area at 66–68°C. The weights of the platinum that are deposited were noted at 1 h intervals and the thickness calculated. The results are presented in Fig. 3. An increase of the platinum concentration in the bath resulted in an increase in the weight of the platinum and, hence, the thickness of deposit. Thus, baths containing 1, 2 and $3\,g\,l^{-1}$ platinum concentrations deposited 2.9, 3.5 and 4.0 μm thick layers in 3 h. The coatings were subjected to most rigorous quenching test by heating up to 600°C, and the coatings were found to be adherent. Fig. 4 represents a scanning electron micrograph of sample deposited from a bath containing $1\,g\,l^{-1}$ of Pt metal. The coating is fine-grained and uniform. The black spots are due to the result of pre-etching treatment of titanium before the deposition. The thickness of the deposits were also checked by XRF technique for confirmation. The values obtained by the XRF method were slightly less than the values calculated from the weight gains during the deposition. This may be due to the fact that the actual area of deposition is $>1\,cm^2$ on sand blasted panels. There is a critical balance between the amount of platinum, reducing and stabilising agents. The ratio of the platinum metal to hydrazine should always be maintained constant, when the baths for higher concentrations of platinum are used; if that is not done, the baths get decomposed. Once started, the decomposition ceases only after all the platinum metal ions are depleted from the solution.

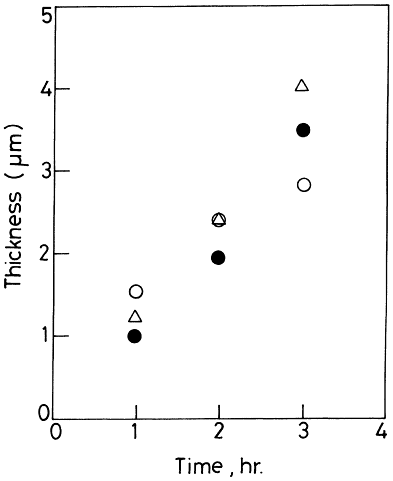

Fig. 3. The effect of platinum concentration in the bath on the thickness of the deposit: (○) 1, (●) 2, (△) $3\,g\,l^{-1}$.

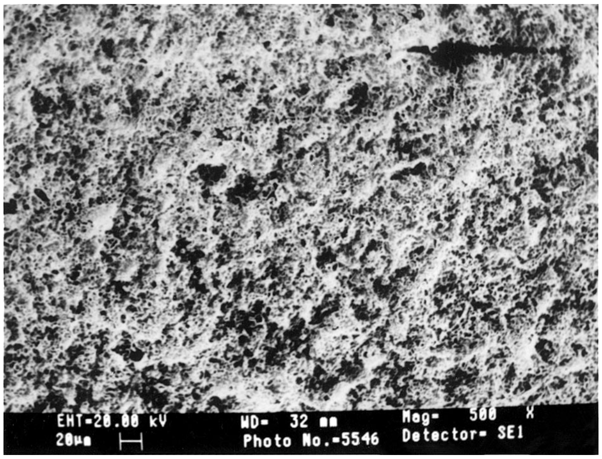

Fig. 4. The scanning electron micrograph of platinum plated (3 h) titanium panel at 500× magnification.

3.3. Deposition on gold plated titanium and titanium powder

The behaviour of deposition on noble metals like gold was also investigated. For this purpose, the titanium panels were first given gold strike and $1\,cm^2$ area of the gold surface was exposed for deposition in a 1-$g\,l^{-1}$ bath. The rate of build up of platinum thickness is shown in Fig. 5. The rate is found to be slower compared to the deposition on pure titanium panel under the same experimental conditions. The deposits were gray, uniform and adherent to the substrate as evident from SEM analysis and quenching tests.

After a duration of 1 h, a 1.1-μm thick platinum layer was deposited on the gold-plated titanium panel, whereas a 1.5-μm thick layer was deposited on pure titanium. This rate is also slower than the reported value of 1.18 μm in 30 min on a pure gold foil by Leaman [6] where the bath was prepared in a different procedure using different additives.

Keeping in view of the importance and use of dispersed platinum materials, as discussed in Section 1, the deposi-

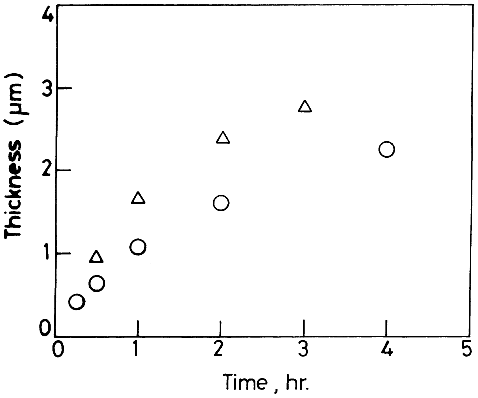

Fig. 5. Comparison of rate of build up of platinum on: (○) gold-plated titanium, and (△) titanium panels. The concentration of the Pt in bath is $1\,g\,l^{-1}$.

Table 1
Data on thickness of Pt on Ti powder (100 mg) from 50 ml of bath solutions

Time (h)	Thickness of layer (μm) at different concentrations of Pt		
	1 (g l^{-1})	2 (g l^{-1})	3 (g l^{-1})
2	0.40	0.66	1.20
3	0.70	0.86	1.25
4	0.72	1.19	1.36

tion of the platinum layers on titanium metal powder was investigated. Titanium metal powder of 300 mesh size was etched in the same way as for the panels for a specific period of time. Then, deposition was effected in electroless baths of 1, 2 and 3 g l^{-1} concentrations. After the deposition was carried out for 2, 3 and 4 h, the powders were filtered. The thickness of the platinum layers were determined by the XRF technique. The results are collected in Table 1. In a 50-ml bath of 1 g l^{-1} platinum concentration, the maximum thickness plated was 0.72 μm in 4 h. The value increases to 1.19 and 1.36 μm when the concentrations of platinum in the bath is increased to 2 and 3 g l^{-1}, respectively. Because of the high surface area of the titanium powder, the average thickness was found to be smaller compared to the thickness on the titanium panels. The use of this platinum dispersed titanium powder as electrocatalyst is to be evaluated.

Applications of this electroless process include plating on titanium panels, titanium powder, gold and other inexpensive core materials. This process can be useful for plating on bio-compatible polymers like polyethylene terphthalate, which can be used as material for implantable electrodes in medical devices [2]. Our preliminary experiments conducted on polyethyleneterphthalate (PET) showed that PET films can be successfully platinum-deposited after metallisation using Pd-DMSO complex solution.

4. Conclusions

The use of an electroless platinum bath to deposit adherent and uniform layers on titanium panels, titanium powder and gold-plated titanium panels is demonstrated. The conditions were optimised for a new set of additives. The effect of concentrations of platinum metal on thickness of the deposit was studied. It was found that the thickness of the deposit increased with increased concentration of the platinum in the bath. The deposition rate on titanium and gold-plated titanium are compared. Platinum coatings on titanium powder were successfully obtained. The applications of the bath are suggested.

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