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Studies of platinum electroplating baths
Part IV: Deposits on copper from Q bath

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The deposition of platinum on copper from a modern commercial electroplating bath (Pt 5Q bath containing 26 mM $Pt(NH_3)_4HPO_4 + \sim 30$ mM sodium phosphate buffer, pH 10.6 at 368 K) has been studied using voltammetry and potential step methods. In addition, polished Cu panels (area 3.4 cm^2) have been electroplated using both constant potential and constant current conditions; current efficiencies have been determined and scanning electron microscopy has been used to show that the morphology of the platinum layers depends strongly on the plating conditions, particularly the potential at which deposition occurs. It is shown that good quality electroplates can be obtained with high current efficiency but a high rate deposition is more readily achieved using controlled potential.

1. Introduction

The Q bath is a modern electroplating bath for platinum, commonly used for coating engineering components which will be exposed to the risk of high temperature corrosion [1, 2]. It is based on a solution of $Pt(NH_3)_4^{2+}$ in a dilute aqueous phosphate buffer, pH 10.3–10.6 and the Pt concentration normally falls in the range 5–20 g dm^{-3}. Satisfactory performance is, however, only obtained when the bath temperature is above 363 K; in these conditions, however, it is possible to obtain high quality deposits at a high current efficiency using current densities in the range 1–10 mA cm^{-2}. Previous papers [3, 4] have emphasized the study of the mechanism of reduction of $Pt(NH_3)_4^{2+}$ in this medium. It has been shown that while $Pt(NH_3)_4^{2+}$ is the only species in solution identifiable by ^{195}Pt NMR (even at 368 K), it is not itself electroactive at potentials positive to hydrogen evolution. It has, therefore, been proposed that the high temperature is required to drive the conversion of $Pt(NH_3)_4^{2+}$ to an electroactive species and it has been postulated that $Pt(H_2O)_4^{2+}$ is possibly the key intermediate.

In this paper we report an investigation of the deposition of platinum on to polished copper substrates from a Pt 5Q bath (the bath containing 5 g dm^{-3} Pt) using potential step and sweep voltammetry and scanning electron microscopy as well as visual observation of the electroplates. Most of the experiments have been carried out in conditions close to those used in the commercial bath and a temperature of 368 K. The area of the substrates plated and the volume of the bath are, however, small compared with commercial systems. Moreover, copper and, indeed, highly polished substrates are seldom encountered in commercial practice.

2. Experimental details

The solution of the Pt 5Q electroplating bath was supplied by Johnson Matthey Materials Technology Division. All experiments were carried out at a temperature of 368 K, using solutions which had been thoroughly deoxygenated with a fast stream of nitrogen gas (BOC Ltd, oxygen free nitrogen).

The instrumentation for electrochemical experiments was a Hitek potentiostat (model DT2101) and function generator (model PPR1) and responses were recorded on an Advance Bryans series 60000 recorder. Voltammetric experiments were carried out in a small glass cell. The copper disc working electrode (area 0.08 cm^2) was fabricated by sealing a copper rod into a glass tube using a film of an epoxy resin. In the cell, the disc working electrode is surrounded by a platinum wire spiral as the counter electrode in the same compartment (volume 20 cm^3) and the reference electrode was in a separate compartment with a Luggin capillary whose tip went into the surface of the working electrode. Throughout, the reference electrode was a commercial Ag/AgCl electrode (Radiometer Ltd) maintained at 368 K. The surface of the copper disc was prepared between experiments by rubbing forcefully on 600 grade emery paper and then polishing with alumina (successively 1, 0.3 and 0.05 μm grades) on a moist polishing cloth (materials from Buehler Inc). Platinum electroplates were prepared on both the copper discs and copper panels (13 mm × 13 mm × 1 mm thick); both were used to prepare samples for scanning electron microscopy while the latter also allowed the determination of current efficiency. The panels were electroplated in an enclosed beaker cell with platinum gauze counter electrodes on both sides of the copper panel. Hence, the area plated was 3.4 cm^2. The panels were degreased with methylene-

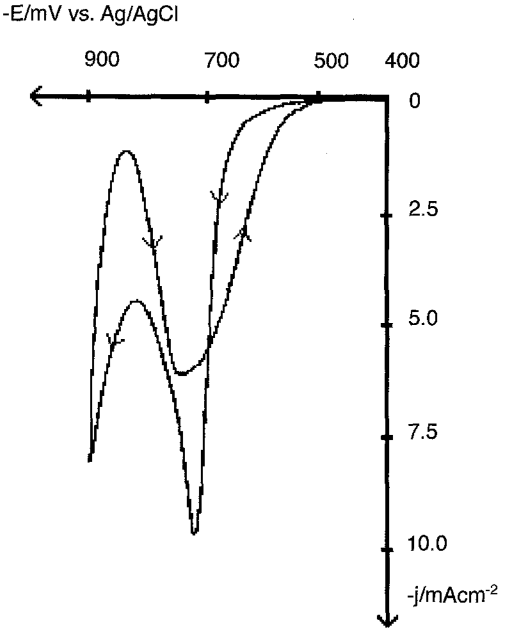

Fig. 1. Cyclic voltammogram for Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6) at a copper disc electrode (area 0.08 cm^2). Temperature 368 K. Potential scan rate 25 mV s^{-1}.

dichloride and then stood in 2 M H_2SO_4 for 30 min before being washed well with deionised water and dried. The scanning electron microscopy was carried out with a Jeol analytical instrument (JSM 6400).

3. Results

No spontaneous deposition of Pt on the copper surface was observed when copper discs or panels were immersed in the Q-bath solution. Indeed, even at 368 K for extended periods of time, the copper surface shows no visible sign of change. Hence, unlike some other Pt(II) solutions (e.g., acidic solutions containing chloride ions [4]), the chemical reactions

$$Cu + Pt(II) \rightarrow Pt + Cu(II)$$

$$2Cu + Pt(II) \rightarrow Pt + 2Cu(I)$$

do not occur when the Pt(II) is present as $Pt(NH_3)_4^{2+}$ in a phosphate buffer, pH 10.4.

Cyclic voltammograms were recorded for the freshly polished copper disc electrode (area 0.08 cm^2) in a solution of 5Q electroplating bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6). Figure 1 reports the response at 368 K. The forward scan shows a sharp and symmetrical cathodic peak at $E_p \sim -740$ mV vs Ag/AgCl; Pt metal can be clearly seen on the copper surface once the electrode potential has been taken into the region of the cathodic peak. Moreover, the peak is not present in phosphate buffer alone and hence it clearly results from the reduction of Pt(II). The peak does not arise through diffusion control. The peak current density of 9.7 mA cm^{-2} is significantly less than the estimated mass transport limited current density in these conditions and the peak height does not depend on the potential scan rate or rotation of the electrode. In any case, the cyclic voltammogram does not have the appropriate shape for a mass transport controlled reaction. In particular, the reverse scan also shows a cathodic peak, although broader and smaller than on the forward scan. The broadness arises because Pt deposition continues to more positive potentials once platinum is present on the surface; initially, on the forward scan, the surface is copper and no reduction of Pt(II) can occur until nuclei of the Pt phase have been created and this process requires an overpotential. In fact, the voltammogram is very similar to that reported earlier with platinum microelectrodes [3, 4] when it was proposed that the decrease in current density negative to the peak results from inhibition of Pt(II) reduction due to the presence on the surface of adsorbed hydrogen atoms [3, 4]. At potentials negative to -850 mV, the current is mainly due to hydrogen evolution.

Potential step experiments were carried out on a polished copper disc electrode in the same solution at 368 K. Figure 2 reports the current density against time responses for a series of potential steps from -400 mV to values in the range from -600 to -700 mV vs the Ag/AgCl reference electrode. It can be seen that following the initial decay of the charging current, the current rises slowly with time until a plateau value is reached. The timescale of the rising current decreases and the limiting current increases as the potential is made more negative. During the initial part of the rising transient, the current density increases as the cube of time; plots of $j^{1/3}$ against t were linear and their slopes increase and the intercepts on the time axis (the induction times) decrease as the deposition potential is made more negative. Hence, the transients have the general form commonly found for metal deposition processes when deposit formation involves a phase nucleation and growth process where nucleation is progressive, the nuclei grow in three dimensions and the thickening of the platinum deposit occurs under kinetic control. Observation of the deposits after the experiments showed that all the deposits were bright and reflecting (although at -600 mV, the deposit was clearly thin) and their adhesion was good, requiring vigorous use of emery paper for their removal. An unusual feature of the transients is the random oscillation of the currents in the plateaux regions of the transients. Their origin is unclear but it should be emphasized that these experiments are carried out at 368 K, close to the boiling point of the electrolyte solution where there is significant thermal convection and gas bubbles regularly nucleate on the solid electrode surface.

It should be noted that these transients are all recorded at potentials in the range positive to the peak on the current/potential curve of Fig. 1. When the current/time transients are recorded over a wider range of potentials, the behaviour becomes more complex. Negative to -750 mV, only a decaying current versus time response is seen but unusually the steady state current decreases as the potential is made more negative. This is clearly seen in Fig. 3 which presents a plot of the steady state current

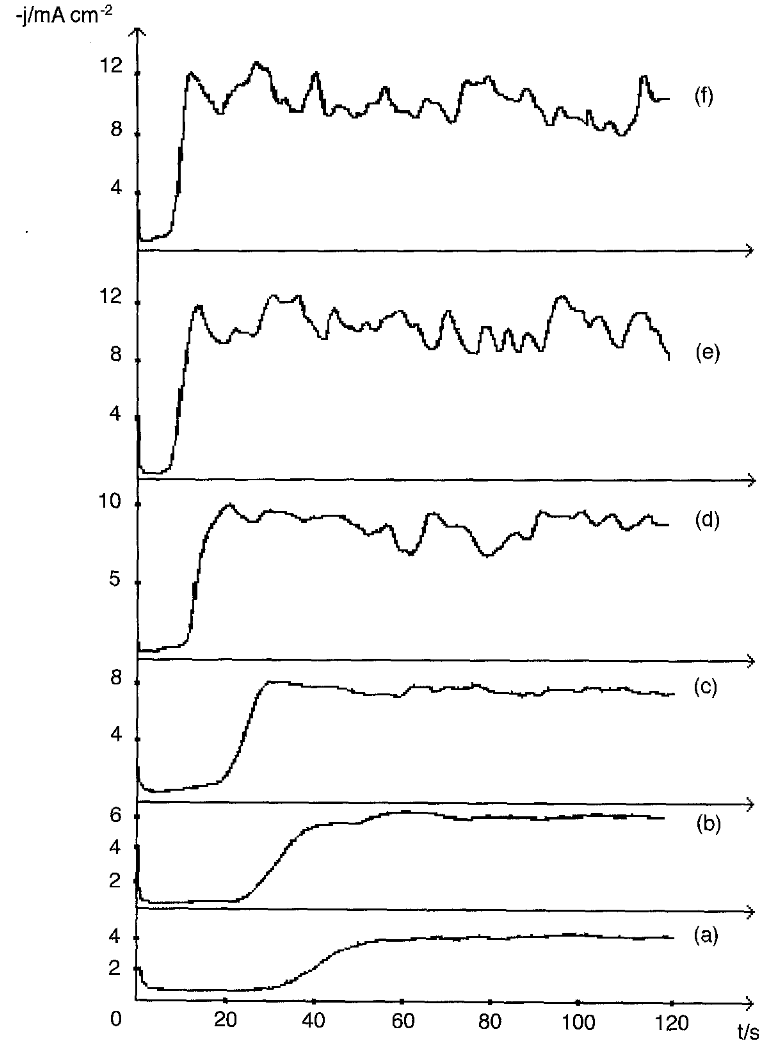

Fig. 2. Current/time transients in response to potential steps from −400 mV to (a) −600, (b) −620, (c) −640, (d) −660, (e) −680 and (f) −700 mV. Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6). Copper disc electrode (area 0.08 cm^2). Temperature 368 K.

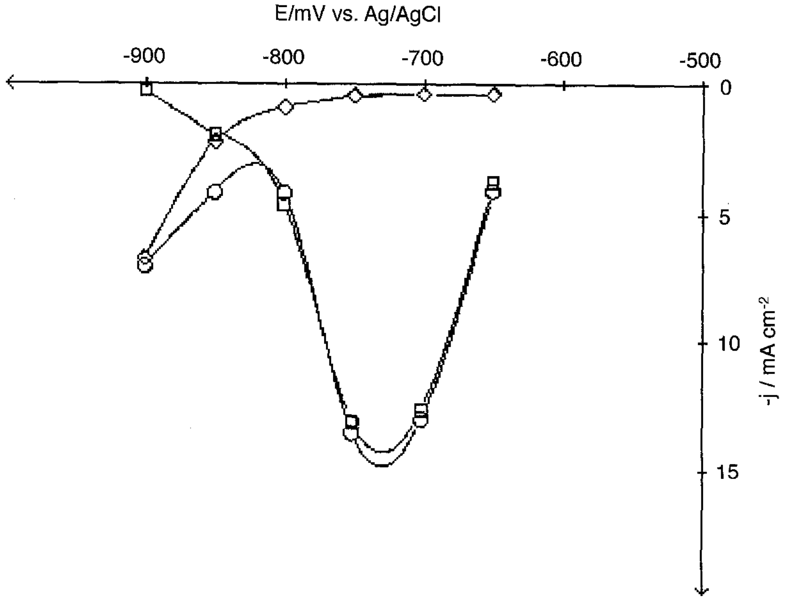

Fig. 3. Plots of steady state current density against potential for Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6) at a copper disc electrode (area 0.08 cm^2). Temperature 368 K. Key: (○) total current density; (□) partial current density for Pt deposition; (◇) partial current density for hydrogen evolution.

Table 1. The properties and appearance of platinum deposits formed at constant current on copper discs from platinum 5Q electroplating solution (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6) at *368 K*

I /mA cm^{-2}	$-E$ /mV vs Ag/AgCl	Q /C cm^{-2}	ϕ^* /%	$v_{Pt}^\dagger$ /μg cm^2 s^{-1}	$L^\ddagger$ /μm	*Appearance*[§]	*Adhesion*
0.5	580	0.1				Complete coverage, metallic and reflecting.	good
1	606	0.1				Complete coverage, metallic and reflecting. SEM shows little structure except imperfections in substrate (e.g., scratches).	good
		1	66	0.64	0.3	Complete layer, metallic and reflecting. SEM just reveals hemispherical substructure. Layer cracked.	good
		10	67	0.64	3	Complete layer, metallic and good highly reflecting. SEM detects no structure but many stress cracks.	good
2.5	620	0.1				At all thicknesses, appearance is metallic and reflecting. SEM reveals no substructure. Layer increasingly cracked with thickness.	good
		1	98	2.4	0.5		
		10	88	2.4	4		
5	880	0.1				Metallic but not highly reflecting tending to grey as layer thickens. SEM shows that a thin layer is structureless, roughness develops and angular crystallites (~ 0.1 μm) appear with thickening.	good
		1	29	1.4	0.15		
		10	18	0.9	1		
10	940	0.1				Metallic but grey. SEM pictures similar to those at 5 mA cm^{-2}.	good
		1					
		10	10	0.9	0.5		

[*] Current efficiency estimated from the weight increase of the cathode.

[†] Rate of Pt deposition from the current density and current efficiency.

[‡] Plate thickness at the end of the deposition from the charge and current efficiency assuming the density of the Pt deposit to be 21.45 g cm^{-3}.

[§] From visual observation and scanning electron micrographs.

density as a function of potential; the steady state curve has a very similar form to the response from the linear sweep experiment, Fig. 1. Hence, inhibition of platinum deposition negative to the peak also occurs in long timescale experiments.

In commercial practice, platinum (as well as all other metals) are plated with the current density as the controlled parameter [2, 3]. Hence, a series of platinum layers were plated at different current densities, j, using the Pt 5Q bath at 368 K. The deposition charge, Q, and hence the deposit thickness, was also varied. In all experiments, the potential quickly settles down to a steady state value and this is reported in the table. The current efficiency, ϕ, for the electroplating reaction was estimated from the increase in weight of the copper panel electrode. The charges consumed, the current densities and the current efficiencies were used to estimate the final thickness of the deposits, L, and the average rate of Pt deposition, v_{Pt}. The electrodeposits were examined by eye as well as scanning electron microscopy and the adhesion of the coating was evaluated both by bending the plated panels, using adhesive tape and abrading the surface with emery paper. The data from these experiments are summarized in Table 1. For current densities of 2.5 mA cm^{-2} and below, deposition occurs at potentials well positive to the peak in the current/potential response (see Figs 1 and 3) and the current efficiency is high. At higher current densities, the potential is markedly negative to the peak in the current/potential response and the current efficiency is significantly lower. Although the adhesion of the deposits is good in all conditions, the appearance of the deposits changes from highly reflecting at low current densities to grey and matt at the higher values. The detailed changes in morphology are clearly seen by scanning electron microscopy. This is illustrated by the two series of experiments using 1 and 5 mA cm^{-2}, see Fig. 4, in which the deposit thickness is varied. At 1 mA cm^{-2}, no structure can be observed for the thinnest deposit (0.1 C cm^{-2} or ~0.03 μm), other than a scratch on the copper substrate. The SEM for the deposit formed with 1 C cm^{-2} shows a very uniform layer but just reveals the hemispherical substructure of the deposit; in addition, a crack in the deposit is obvious. The SEM for the thickest layer (10 C cm^{-2} or ~3 μm) again shows a very uniform deposit with no substructure but even more extensive cracking has occurred. The photograph shows that these cracks result from shearing of the layer and therefore that the deposits are highly stressed. Stress in precious metal electroplating is recognised as a common problem. The same series of experiments with electrodeposition at 5 mA cm^{-2} leads to quite different results. The SEM photographs show that no cracking occurs and the layers remain uniform but with increasing thickness, the deposit becomes rougher and the thickest layer (~1 μm) can be seen to be made up of small, angular crystallites. It is therefore not surprising that this deposit appears to be only poorly reflecting. It should be noted that the highest plating rate was observed with the current density of 2.5 mA cm^{-2}, when platinum is deposited at a rate of 2.4 μg cm^{-2} s^{-1}.

A series of platinum deposits were grown potentiostatically on to copper discs from the Pt 5Q solution at a temperature of 368 K. Again, after an initial transient response, the steady state current is reached within 100 s and the observed steady state current densities are reported in Table 2 along with estimates of the current efficiencies. The appearance and adherence of the deposits were noted and their morphology examined using scanning electron microscopy. In this

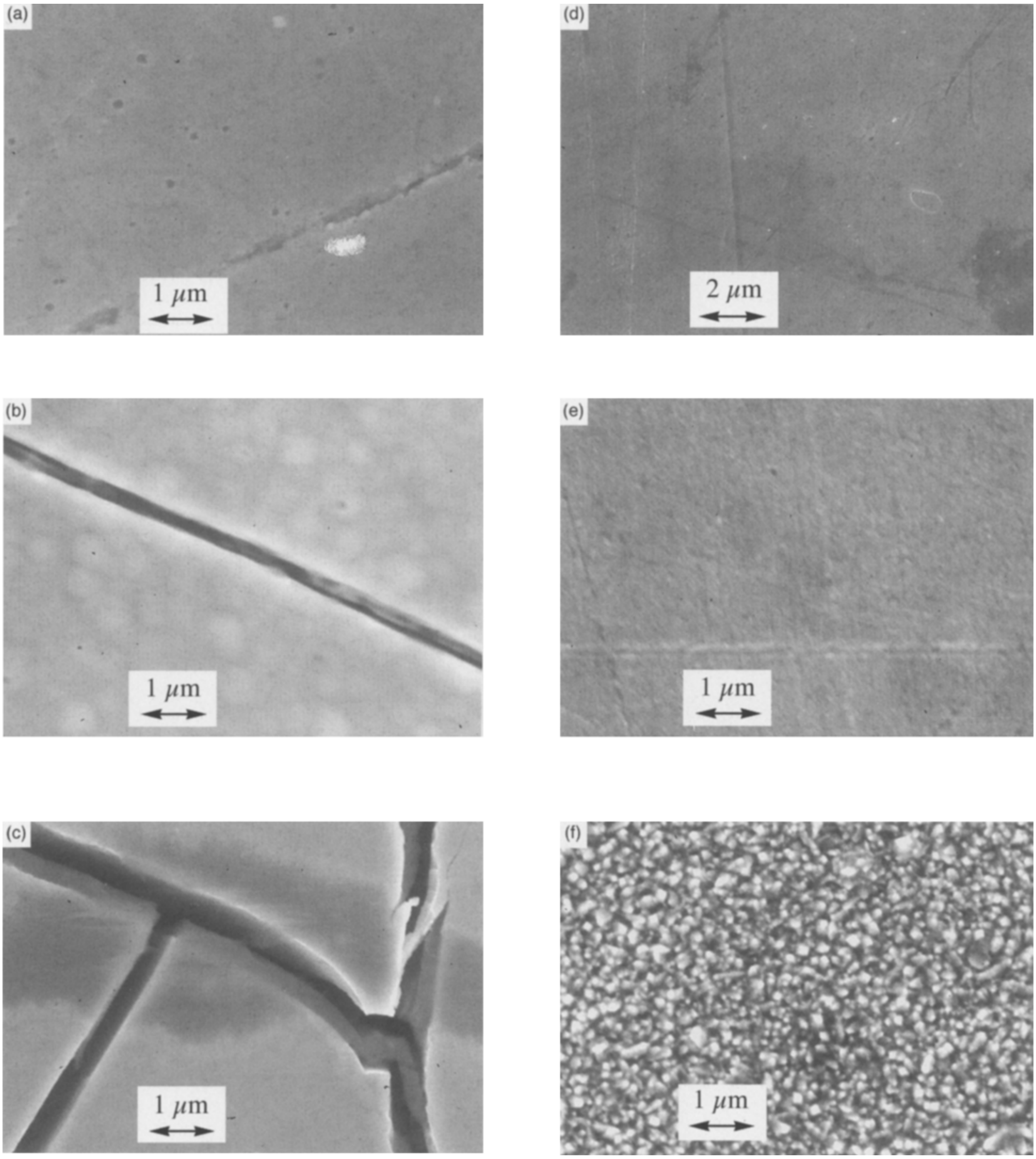

Fig. 4. Scanning electron micrographs for platinum coatings on copper deposited at constant current. Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6). Temperature 368 K. (a) 0.1, (b) 1 and (c) 10 C cm^{-2} layers all deposited at 1 mA cm^{-2}. (d) 0.1, (e) 1 and (f) 10 C cm^{-2} layers all deposited at 5 mA cm^{-2}. Other conditions see Table 1.

series of experiments, it quickly became apparent that it was possible to deposit thick layers of platinum at high rates while maintaining highly reflecting finishes and hence the depositions were continued for very extended periods of time, 80–160 min, so as to form very thick coatings (usually 10–25 μm). In such experiments, the current is constant throughout almost all the deposition (i.e., except for the short, initial period). The steady state current densities and current efficiencies may be used to construct a plot of the partial current densities for platinum deposition and hydrogen evolution versus potential and these data have been added to Fig. 3. It can be seen that the partial platinum deposition current density against potential curve has an identical form to the steady state voltammogram in the same conditions. It should also be recognized that the current efficiency remains high well beyond the peak and into the minimum in the current/potential curve; hence, a change in the major electrode reaction is not the cause of the decrease in current. Indeed, it is evident that the decrease in current density results only from inhibition of the platinum deposition reaction. It can further be seen that by controlling the potential at −750 mV, the deposition rate reaches 12.9 μg cm^{-2} s^{-1}, more than five times the maximum rate achieved with constant current control. Moreover, the deposit quality is high.

SEMs for the deposits at four potentials are shown

Table 2. The properties and appearance of thick platinum deposits formed potentiostatically on to copper discs from platinum 5Q electroplating solution (26 mM $Pt(NH_3)_4HPO_4 + \sim 30$ mM sodium phosphate buffer, pH 10.6) at 368 K

$-E$ /mV vs Ag/AgCl	I /mA cm^{-2}	Q /C cm^{-2}	ϕ^* /%	$v^{\dagger}_{Pt}$ /μg cm^2 s^{-1}	$L^{\ddagger}$ /μm	*Appearance*§	*Adhesion*
650	4.1	40	92	3.7	13	Bright but matt appearance, uniform cauliflower morphology with many cracks.	poor
700	13.1	66	97	12.4	23	Bright and reflecting, little structure but many cracks.	fair
750	13.6	66	97	12.9	23	Very bright and reflecting, uniform very small crystallites, a few cracks.	good
800	4.4	40	79	3.4	11	Semibright, larger but uniform crystallites, no cracks.	very good
850	4.4	40	46	2.0	6	Semibright, large and uniform crystallites, no cracks.	good
900	7.2	66	4	0.3	1	Matt black, uniform layer no cracks.	good

Footnotes *, †, ‡ and § are explained on Table 1.

in Fig. 5 and observations about the morphology are summarized in Table 2. It can immediately be seen that the deposit morphology varies strongly with the deposition potential. At −650 mV, the deposit has the cauliflower structure typical of many high performance electroplates and it seems to consist of many overlapping hemispheres with sizes between 0.5–2 μm. The micrograph also, however, shows some cracks and the deposit shows rather poor adhesion; it is clear that the layer is highly stressed. This is, as noted above, normal, for precious metal deposits which have a thickness $\gg 1$ μm and, indeed, it is unusual to put down such thick layers of platinum. At −700 mV and −750 mV, potentials close to the peak in the current/potential response, the deposits are shiny and highly reflecting and the micrographs of the platinum layers show very little structure. The deposits appear to consist of tightly packed, very

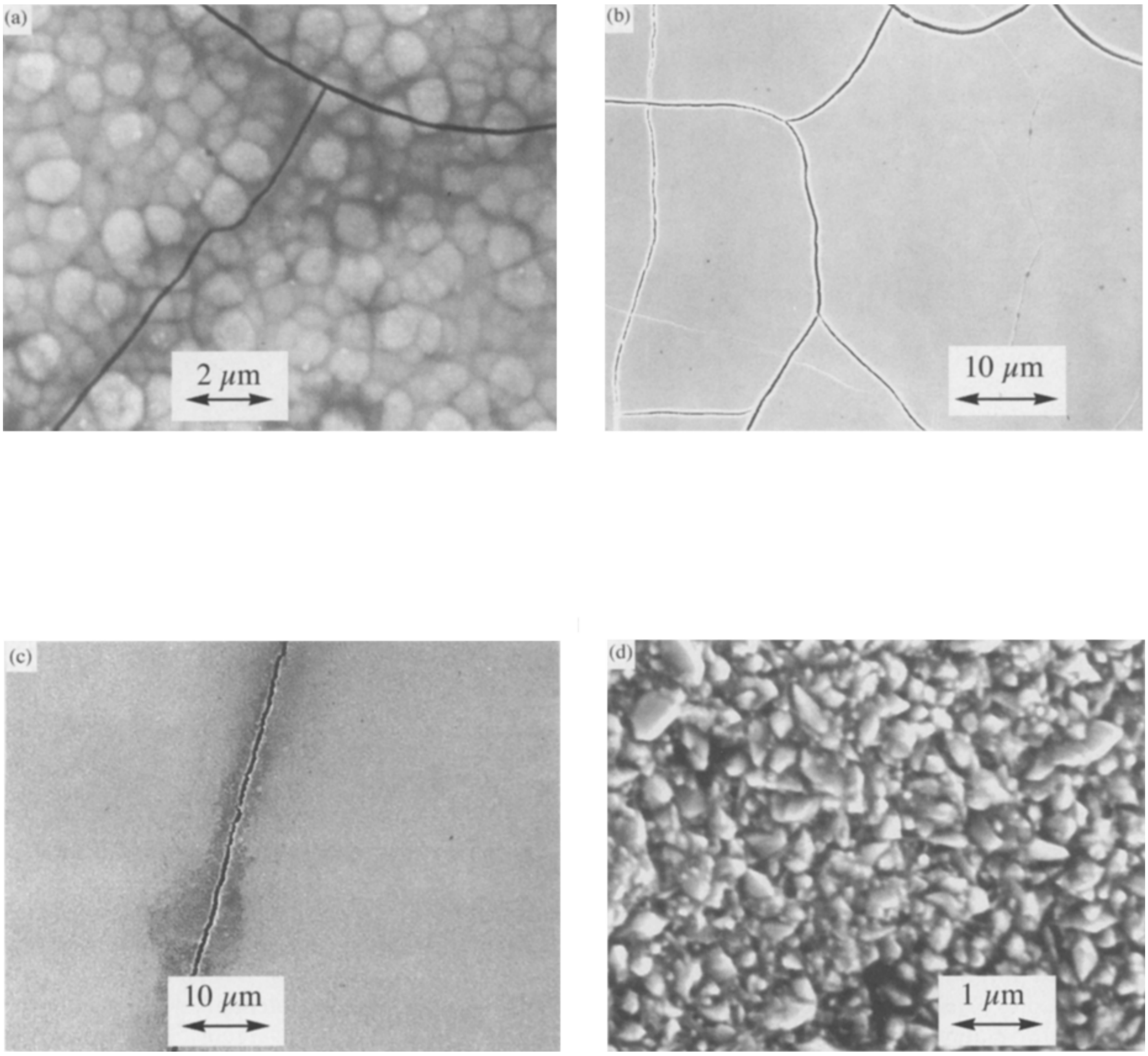

Fig. 5. Scanning electron micrographs for thick platinum coatings on copper formed at constant potential. Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4 + \sim 30$ mM sodium phosphate buffer, pH 10.6). Temperature 368 K. Deposition potentials were (a) −650, (b) −700, (c) −750 and (d) −850 mV. Other conditions see Table 2.

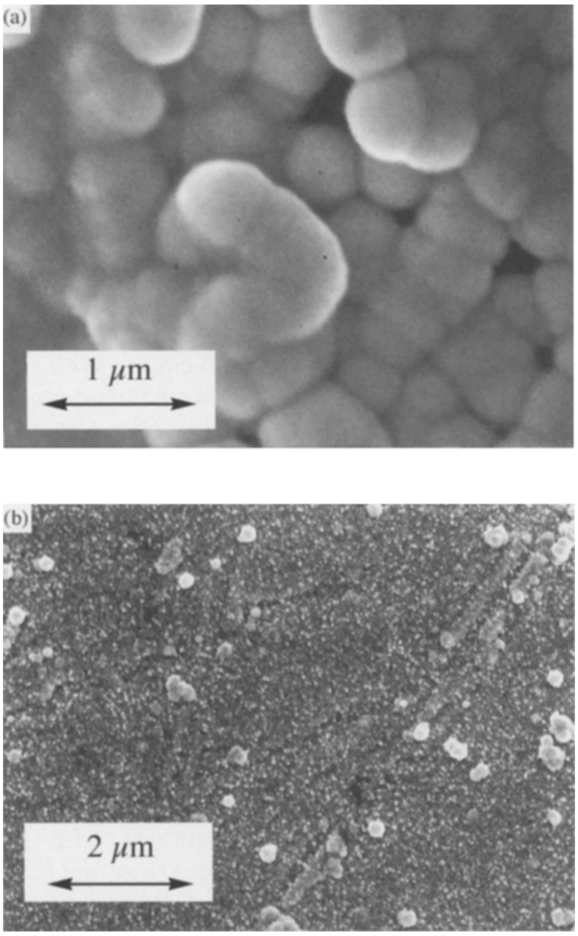

Fig. 6. Scanning electron micrographs for thin platinum coatings on copper formed at constant potential. Pt 5Q bath (26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6). Temperature 368 K. Deposition conditions were (a) 2.4 C cm^{-2} at −700 mV and (b) 1.8 C cm^{-2} at −825 mV.

small crystallites. Moreover, as the deposition potential is made more negative, the adhesion is improved and the density of cracks decreases. At more negative potentials, the morphology changes totally, the micrographs show angular grains, dimensions ~0.5 μm. The appearance is metallic but only semibright but the signs of stress have disappeared; there are no cracks and the adhesion is very good. The current efficiency is moderate. With the commencement of significant hydrogen evolution, the current efficiency drops and the deposit becomes increasingly matt.

Thinner layers (0.5–1.2 μm) of platinum were also deposited potentiostatically on to both copper discs and plates. Because the transient effects during the initial stages of nucleation and growth occur on a timescale which is very short compared to the plating time, the current densities operative during almost all of these depositions is the same as used in the preparation of the thick deposits. Positive to −800 mV, the deposits were always highly reflecting. Moreover, the adhesion was good and for these thin deposits there was never evidence of cracking. The thin deposits did, however, retain some evidence of the surface preparation; any scratches on the copper led to some alignment of the metal nuclei along the scratch. The SEM of a platinum layer formed at −700 mV on a carefully polished surface showed that the deposit was made up of a large number of overlapping hemispherical centres, diameters ~0.2 μm, see Fig. 6(a). Again, however, the deposits formed negative to −800 mV, see Fig. 6(b), was quite different and the layer is composed of much smaller and angular crystallites.

4. Discussion

It has been confirmed that the electroplating bath consisting of 26 mM $Pt(NH_3)_4HPO_4$ + ~30 mM sodium phosphate buffer, pH 10.6 (known as a Pt 5Q bath) allows the deposition of adherent and highly reflecting platinum coatings with a high current efficiency when the bath is operated at 368 K.

It has also been demonstrated that the morphology of the platinum electroplates is determined by the potential of deposition. The steady state current/potential response for the electrode reaction Pt(II) → Pt is peaked due to inhibition of the Pt(II) → Pt process in the potential range just positive to hydrogen evolution and it has been suggested [3, 4] that it is adsorbed hydrogen which inhibits the deposition. The behaviour of the deposition reaction certainly seems to reflect the shape of this curve:

(a) At potentials positive to the peak, current/time transients are typical of those for a nucleation and growth process and the rising portion can be fitted to a model of progressive nucleation and three dimensional growth of the nuclei under electron transfer control. Moreover, SEM shows the platinum layer to be constructed from a large number of small, overlapping hemispheres. The deposits are very reflecting but highly stressed and they crack as the coating is thickened.

(b) At slightly more negative potentials, the SEM photographs show the deposits to be almost featureless although they may still consist of very small hemispherical centres. Such structures still appear metallic and highly reflecting but are less stressed since cracking is less frequent even with the thicker coatings. They also show the strongest adherence to the copper substrate. Furthermore, these favourable deposits may be deposited at a high rate (13 mA cm^{-2}) with high current efficiency but are only easily formed using potential control. The potential step experiments show only a falling current/time response in this region and some inhibition of Pt(II) reduction seems already to be occurring.

(c) At even more negative potentials, the electrodeposits are rougher and when thick are shown to have a quite different morphology, consisting of angular crystallites. They show no tendency to crack but appear matt and rather poorly reflecting.

It is interesting to speculate the reasons for these three types of deposit morphology. The potential ranges correspond to clean platinum, platinum covered with strongly adsorbed hydrogen and platinum covered by weakly as well as strongly adsorbed hydrogen. It is not possible to confirm whether this is the determining factor.

When the plating is carried out using a constant current, the deposit morphology and properties are still determined by the potential which is taken up by the electrode. Because of the peaked nature of the current/potential response, using a constant current it is only possible to achieve stable potentials which correspond to very positive or very negative potentials and, hence, only deposits of type (a) and (c) can be observed.

In fact, although perhaps difficult to achieve on a technical scale, constant potential deposition seems to have considerable advantages compared to the normal constant current deposition. Type (b) deposits appear to be superior to type (a) formed in commercial practice especially if it is desirable to form thick coatings ($> 5\,\mu$m) without stress or cracks. Certainly, using a constant potential, it was possible to form reflecting deposits with a high current efficiency at 13 mA cm^{-2}. With constant current control, the most similar deposits were obtained with current densities of 2.5 mA cm^{-2}. These correspond to plating rates of 12.9 and 2.4 μg cm^{-2} s^{-1}, respectively. Hence, constant potential had a rate advantage of about five. This was turned to advantage in depositing 23 μm coatings with essentially quantitative current yield. Recent commercial practice has been to use plating baths containing 20 g dm^{-3} of Pt(II) in order to allow accelerated deposition. A change of control strategy might offer a cheaper alternative, at least for substrates with simple geometry.

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