Studies on the Deposition Behavior of Pt[(NH₃)₂(H₂O)]⁺² Complex Bath

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The electrodeposition behavior of platinum from the Pt[(NH₃)₂(H₂O)]⁺² complex bath was investigated on copper and titanium panels and the deposits were characterised by SEM, XRF and XRD techniques. The current efficiencies for the deposition process were examined. The bath deposits bright and adherent coatings. The bath operates at lower temperatures than the Q-bath.

Keywords: Electrodeposition, pre-electrolysis, polarization, ligand substitution

Introduction
Platinum is extensively used as a coating material onto the activation components, turbine blades, electrodes, electronic components and jewellery to impart corrosion resistance or pleasing appearance. Platinum electroplating is usually carried out using baths based on P-salt or Q-salt. However, these baths suffer from certain drawbacks such as high operating temperature and low plating current densities. These limitations lead to the explorations in the developments of new baths based on Pt[(H₂O)₄]⁺² complex species [1]. The present study describes the results on the plating behavior of bath derived from cis-Pt[(NH₃)₂(H₂O)]⁺² complex solution. The techniques like Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) techniques and X-Ray Fluorescence (XRF) were used to characterise the deposited coatings.

Experimental
The complexes cis-Pt[(NH₃)₂(I)]⁺² and cis-Pt[(NH₃)₂(H₂O)]⁺² were prepared by a known procedure after some modifications [2]. K₂PtCl₆ (0.5 g, 1.2 mM) was dissolved in 50 ml of water and aqueous HCl (5.2 mM) was added while stirring. A dark brown solution was formed after 10 minutes. To this, NH₄Cl (2.5 mM) and 1 ml of 50% aqueous ammonia were added with stirring. After a period of 15-20 minutes, the complex cis-Pt[(NH₃)₂(I)]⁺² was precipitated as a mustard colored material. This was filtered, washed with cold distilled water and dried at room temperature. This cis-Pt[(NH₃)₂(I)]⁺² complex (0.350 g, 0.72 mM) was dissolved in 100 ml of distilled water by heating to 343 K. To this AgClO₄ (0.298 g, 1.44 mM) in water was added slowly over a period of one hour. The heating and stirring was continued for two more hours after that, the precipitated AgI was filtered off to get a clear colorless solution of cis-Pt[(NH₃)₂(H₂O)]⁺²ClO₄ of 3.30 g/l concentration. The excess Ag⁺ was removed by pre-electrolysis at 0.25 V (vs. SCE) using large platinum foils until there are no further black deposits of silver metal on the cathode.

The plating experiments were performed on copper and titanium panels of exposed area of 1 cm x 2 cm for a period of 0.5 to 1 hr in 100 ml cell using Pt foil as the anode. Copper panels were electrocleaned in alkaline cleaner and titanium was chemically cleaned in conc. HCl containing some HF. The pH of the bath was adjusted to 10 by the addition of Na₂HPo₄ (0.78 mole) with dil. NaOH solution. The thickness of the platinum deposits was determined by XRF method using Coating Measurement Instruments [CMI] of type XRX-XYZ and the measurements are accurate by +/- 0.001 microns. SEM was recorded on Hitachi S-300 H instrument and the XRD spectra were recorded by using a JEOL instrument.

Results and discussion
It is well known in the literature that the electroactive species in the plating baths containing Pt[(NH₃)₂]⁺² complex is not simply Pt[(NH₃)₄]³⁺, when the plating is carried out at temperatures between 363 - 368 K, but Pt[(NH₃)₄(H₂O)]⁺² (where x = 1 - 3) [3]. At these high temperatures, it was suggested that,
there will be a ligand substitution reaction in the original platinum complex by water molecules. As the substitution at Pt centers is known to be slow it is necessary to have higher temperatures for a faster ligand substitution [4,5]. Hence the plating baths should have such high working temperatures and this working temperature can be significantly reduced when complexes of the type $\text{Pt}([\text{NH}_2]_2\left([\text{H}_2\text{O}\right]_x)_2 x = 1 - 4)$ are used. This is indeed demonstrated in the present investigation, as only 343 K temperature is needed (compared to 363 - 368 K) for an acceptable deposition. The most likely mechanism in the deposition process can be

$$\text{Pt}([\text{NH}_2]_2\left([\text{H}_2\text{O}\right]_x)_2 x = 1 - 2) + 2e^- \rightarrow \text{Pt}^0$$

The polarization behavior for the electrodeposition of platinum on copper and titanium electrodes are shown in Figs.1 and 2 respectively. The current efficiency of the bath was examined on copper panels at temperatures 333, 343, 353 and 363 K, at a current density of 0.5 mA/cm$^2$. The results showed that a maximum efficiency of 72% could be obtained at 343 K, after which the efficiency decreases with increase of temperature. The thickness obtained was 0.56 micron at these conditions within half-an-hour plating time. The data are collected in Table 1. The deposits are bright and adherent to the substrate. Fig. 3 shows the optical micrograph of 0.5-micron thick platinum deposit. Owing to its lower thickness, a proper XRD spectrum of this coating was not obtained. The efficiency of the bath was also checked at various current densities, viz., 1, 2 and 3 mA/cm$^2$ for one hour at 343 K (Table 1). The results showed that the efficiency decreased with current density, but the deposits are still bright and adherent.

**Table 1. Data on platinum deposition on copper.**

<table>
<thead>
<tr>
<th>C. D (mA/cm$^2$)</th>
<th>Temp. (K)</th>
<th>C. E. (%)</th>
<th>Thickness (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>333</td>
<td>39</td>
<td>0.37</td>
</tr>
<tr>
<td>0.5</td>
<td>343</td>
<td>72</td>
<td>0.56</td>
</tr>
<tr>
<td>0.5</td>
<td>353</td>
<td>50</td>
<td>0.41</td>
</tr>
<tr>
<td>0.5</td>
<td>363</td>
<td>44</td>
<td>0.36</td>
</tr>
<tr>
<td>0.5</td>
<td>343</td>
<td>72</td>
<td>0.56</td>
</tr>
<tr>
<td>1</td>
<td>343</td>
<td>50</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>343</td>
<td>20</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>343</td>
<td>10</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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The plating behavior of the bath was also investigated on titanium substrates. The data is summarized in Table 2. The maximum current efficiency of 90 % is obtained when the current density is 0.5 mA/cm². Further increase in current density resulted in decline of efficiency. The coatings were bright and adherent, but less bright compared to coating on the copper panel. SEM analysis of the above deposit shows that coating is uniform. Under higher resolution, the structure showed a cauli-flower type surface morphology. The scanning electron micrographs are shown in Figs. 4 and 5. XRD spectrum was also recorded. The XRD pattern has indicated that polycrystalline film of platinum with plane orientations (111), (200), (220), (311) and (222) were deposited.

Table 2. Data on platinum deposition on titanium panel.
Concentration of bath = 3.5 g/l of Pt.,
Time = 1 h, pH = 10.4 and
Temperature = 343 K

<table>
<thead>
<tr>
<th>C.D. (mA/cm²)</th>
<th>C. E. (%)</th>
<th>Thickness (micron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>90</td>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
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<td>3</td>
<td>7</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Conclusion**

The electrodeposition behavior of platinum from the Pt[(NH₄)₂(H₂O)₂]²⁺ complex bath was investigated and SEM and XRD techniques were used to characterize the deposits. The current efficiencies for the deposition process on copper and titanium panels were found to be decreased as the current density is increased. The bath deposits are bright and adherent. The bath operates at lower temperatures than the Q-bath.

**References**