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To cite this version:
M. Leisch, K. Rendulic. ATOM PROBE ANALYSIS OF ADDITION AGENT BEHAVIOR IN ELECTRODEPOSITION. Journal de Physique Colloques, 1984, 45 (C9), pp.C9-477-C9-481. <10.1051/jphyscol:1984979>. <jpa-00224468>

HAL Id: jpa-00224468
https://hal.archives-ouvertes.fr/jpa-00224468
Submitted on 1 Jan 1984

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ATOM PROBE ANALYSIS OF ADDITION AGENT BEHAVIOR IN ELECTRODEPOSITION*

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Résumé - Nous avons réalisé une analyse à l'aide d'un spectro-mètre à temps de vol pour déterminer de quelle manière et dans quelle mesure des molécules organiques, ajoutées par électrolyse sont incorporées dans des dépôts galvaniques de platine. En plus de la détermination de la quantité totale de substance organique déposée avec le métal, la concentration relative de différents fragments moléculaires nous donne une information supplémentaire sur le mode d'inhibition.

Abstract - We have performed a TOF atom probe analysis to determine in which manner and to what extent organic agents added to the plating solution are incorporated into platinum electrodeposits. From the type of molecule fractions incorporated one can gain information about the particular process of inhibition involved.

The addition of organic substances as levelling- or brightening agents to the plating solution is a frequently used technique to obtain technologically desirable features of electrodeposits. It is generally assumed that by the addition-agent during crystal growth, active sites for nucleation are blocked. The consequence is an increased overvoltage resulting in the growth of smaller and more uniform crystal grains. During the plating process, the addition agents are partially changed or even included in the electrodeposit. Experiments to investigate the incorporation of organic matter were mostly concerned with obtaining estimates for the total amount of substance enclosed. Some methods can give direct results (radioactive tracers); some methods use rather indirect means (decrease of addition agent in the solution, change in resistivity of the deposit).

We have performed a TOF atom probe analysis to determine to what extent the addition agents are incorporated into platinum electrodeposits. The analysis was carried out in a computer controlled imaging type atom probe /1/. All experiments have been performed under UHV-conditions.

Organic substances, coumarin and p-toluenesulfonamide both frequently used organic inhibitors, were added to the plating solution (Pt-DNS-solution from Johnson & Matthey, GB.) in concentrations similar as used in technical processes (0.2 - 0.6 mMol).

As base material for the platinum electrodeposits, iridium and tungsten specimen were used /2,3/. The plating was performed under AC current and slight agitation. The temperature of the bath was kept at 40 C.

*Supported by the "Fonds zur Förderung der wissenschaftlichen Forschung"
The concentration of organic matter enclosed into the deposit has to be compared to a reference concentration obtained for the "clean" electrodeposits. Into the electrodeposits prepared without addition agents, mainly N, O and S (originating from components of the electrolyte) are incorporated /4/. About 2.5% of the particles registered are contaminants, excluding hydrogen.

Coumarin is a frequently used brightening agent. In our investigation it was added to the plating solution in a concentration of 0.1 g/l. Infrared spectroscopy of a freshly prepared solution indicates that most of the coumarin is immediately changed to melilotic acid. To aid further discussion, the structure of both coumarin and melilotic acid is depicted in fig.1.

![Fig.1 - Structural formulas of coumarin and melilotic acid (right)](image)

Mass numbers marked with (s) indicate species only detected on the surface of the deposit.

In the analysis of the electrodeposit, three distinctly different regions are encountered: the surface region, the bulk deposit and the interface to the base material. The concentrations of contaminants in these three regions are compiled in the table below. Organic materials can dissociate into a large variety of fractions depending on the number of hydrogen atoms retained or lost. For this reason the mass signals have been separated into appropriate mass intervals. Not mentioned in the table are compounds of the base material (W-O, W-C) detected at the interface /4/.

The largest fraction of particles detected are smaller than 54 amu. Only on the surface larger fractions of the molecule and even complete coumarin molecules are seen. A loss of the CO group in coumarin would result in mass 118 which indeed is detected on the surface. Mass signals in the range of 74 to 79 correspond to the relatively stable benzene ring which is obtained after the loss of OH and CH₃CH₂HCO₂ from the molecule of melilotic acid. As with any mass spectroscopic analysis there is the question at what point the break up of the molecule occurs. Since platinum is a good catalyst most of the cracking will probably occur before desorption. Some dissociation will, of course, happen during field desorption.
Table - Average concentration of the main organic fragments detected in platinum electrodeposits

<table>
<thead>
<tr>
<th>Mass (amu)</th>
<th>Mass Compound</th>
<th>Coumarin added to plating solution</th>
<th>p-Toluenesulfonamide added to solution</th>
<th>Plating solution without addition as reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Surface</td>
<td>Bulk</td>
<td>Interface (^1)</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>2.8</td>
<td>2.5</td>
<td>1.5</td>
</tr>
<tr>
<td>14-16</td>
<td>N, CH(_n), O, NH(_2)</td>
<td>5.1</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>25-29</td>
<td>CO, COH, C(_2)H(_n)</td>
<td>7.5</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>37-45</td>
<td>CO(_2), CH(_0)O, C(_2)O, C(_3)H(_n)</td>
<td>5.0</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>49-54</td>
<td>C(_3)OH, C(_4)H(_n)</td>
<td>2.0</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>59-66</td>
<td>SO(_2), C(_4)OH, C(_5)H(_n)</td>
<td>0.3</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>74-79</td>
<td>C(_6)H(_n), C(_3)H(_6)O(_2)</td>
<td>0.5</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>89-92</td>
<td>C(_7)H(_n)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>106-108</td>
<td>C(_6)H(_n)O(_2), C(_7)H(_n)O</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>118-119</td>
<td>C(_8)H(_6)O, C(_7)H(_n)O(_2)</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>146</td>
<td>C(_9)H(_6)O(_2)</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>171</td>
<td>C(_7)H(_9)NSO(_2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) on iridium base material
\(^2\) on tungsten base material
In the bulk platinum deposit one mostly registers the masses 25-29, 37-45 and 49-54. Large fragments, as found in the surface region, are completely absent. It is, of course, no surprise that a large amount of atomic carbon is found: this is the last product in the cracking process of the CH chain of the melilotic acid or even from the benzene ring. Most of the signals in the range 25-29 amu originate from CO which is also found for the "clean" electrodeposits. The fragments in the range 37-45 can be interpreted to be CHO\(_2\), C\(_2\)O, C\(_2\)OH or C\(_3\)H\(_n\) (see fig.1). Finally the largest amount of cracking products appear between 49 and 54 amu. Most likely these signals correspond to C\(_3\)OH from the chain of the melilotic acid and possibly C\(_4\)H\(_n\) as a remains of the benzene ring.

From the table one can also recognize that at the interface to the base material there is a somewhat enhanced concentration of contaminants. As compared to the bulk deposit slightly larger fragments are detected. Interfaces between the electrodeposit and a smooth field-evaporated base material show fewer inclusions than the boundary on a rough, freshly etched needle (which seems an obvious result). After removal of almost all platinum from a rough iridium surface we can still register signals from the benzene ring, C\(_4\)OH and C\(_5\)H\(_n\). This would indicate that some molecules (or fractions thereof) were originally adsorbed on the iridium and subsequently covered by platinum.

Looking at all the observed cracking products, the question arises if they add up to known stoichiometry. Actually, most of the detected particles incorporated in the bulk deposit can be explained as a part of the substituted chain of the melilotic acid molecule. It can be assumed that the remaining benzene ring reacts with the cathodically formed hydrogen and will be desorbed and solvated. Only a small quantity of benzene seems to be completely cracked. There is also a noticeable deficit of oxygen in the organic matter detected. The most likely explanation is that some of the melilotic acid loses oxygen in form of OH or CO\(_2\) which remains in the solution.

In addition, we also investigate the behaviour of p-Toluenesulfonamide in platinum deposits. Generally speaking, the results are quite similar as in the case of coumarin. The cracking products detected are, of course, somewhat different (for the structure of the molecule see fig.2).

\[
C_7H_9NSO_2
\]

Fig.2 - Structural formula of p-toluenesulfonamide (s) denotes that these species are only detected on the surface of the platinum electrodeposits.
On the surface no complete molecules could be registered. The loosely bound sulfonamide group could be removed by catalytic cracking as well as by the process of field desorption. What is left is a compound C7Hn which is detected in the range of 89-92 amu. The incidence of signals near 64 amu indicates the presence of SO2 from the sulfonamide chain.

In the bulk of the deposit, again the stoichiometry for the cracking products is not retained. Signals around mass 64 and 16 have a too high concentration. That means that the ring structure is not as easily incorporated as the sulfonamide group.

One has to point out that for the process of inhibition, the adsorption of the aromat and not the incorporation into the deposit is a necessary condition.

One last word concerning the total mass of organic matter enclosed into the deposits. For the concentrations in the solution used, the mass of about 0.5 to 1 molecule is incorporated together with 100 platinum atoms.

References