SHORT COMMUNICATION

The surface energy of disperse cadmium electrodeposits formations

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(Received 15 April 2004)

Abstract: The surface energy of disperse cadmium electrodeposits formation was determined by using a procedure described earlier. It was shown that the surface energy strongly depends on the composition of the solution from which the deposition was carried out.

Keywords: electrodeposition, cadmium, disperse cadmium formation, surface energy.

INTRODUCTION

The surface energy of disperse copper electrodeposit formation in acid sulfate solutions was determined as 2.7 ± 0.3 J cm⁻². On the basis of this value it was possible to estimate the specific surface of the copper powders. On the other hand, this value is much larger than the surface tension estimated for solid metals in vacuum, and probably includes all energetic requirements for disperse copper electrodeposition.

The aim of this work was to apply a procedure described earlier in the case of disperse cadmium electrodeposition from different solutions and determine whether it does or does not depend on the composition of the solution.

EXPERIMENTAL

The electrodeposition of cadmium was performed potentiostatically from two different solutions: sulfate (0.1 M CdSO₄ + 0.5 M H₂SO₄) and ammonium (0.1 M CdSO₄ + 0.1 M (NH₄)₂SO₄), onto a stationary wire electrode. The cadmium wire electrode was prepared in two steps:

1st step – deposition of copper onto the platinum wire electrode, from a solution 0.1 M CuSO₄ + 0.5 M H₂SO₄, overpotential 200 mV, duration 3 min;

2nd step – deposition of cadmium from sulfate (0.1 M CdSO₄ + 0.5 M H₂SO₄, overpotential 20 mV, duration 3 min) or ammonium solution (0.1 M CdSO₄ + 0.1 M (NH₄)₂SO₄, overpotential 100 mV, duration 3 min), onto a platinum wire electrode that had already been plated with copper.

After relaxation of the electrode diffusion layer for 15 min, the overpotential was adjusted to 20 mV and the current, I₂₀, was measured. The overpotential was then adjusted to a desired value, η, and the deposition of cadmium was carried out. After the required quantity of electricity had been

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reached, the overpotential was set to zero and electrode was relaxed for 15 min. Then the overpotential was adjusted again to 20 mV, and current, \( I_{20,\eta} \) measured. One experiment includes deposition of the same quantity of cadmium at two overpotentials \( \eta_1 \) and \( \eta_2 \). 

Polarization curves were determined from both cadmium containing solutions. 

The energy for the disperse deposition was determined according to the formula\(^2\):

\[
\gamma = \frac{\eta_2 - \eta_1}{I_{\text{lim}}} \int_0^t I dt
\]

where \( \eta_2 \) and \( \eta_1 \) are the deposition overpotentials being within the limiting diffusion current density range, \( \int_0^t I dt \) is the quantity of electricity, \( S_2 \) is the surface of the electrode with cadmium deposited at a higher overpotential, \( \eta_2 \), and \( S_1 \) is the surface of the electrode with cadmium deposited at a lower overpotential, \( \eta_1 \).

The quantity of electricity was determined by graphical integration of the \( I - t \) dependence, recorded during the deposition.

The surfaces of deposited cadmium at overpotentials \( \eta_2 \) and \( \eta_1 \) can be calculated according to the equations:

\[
S_2 = S_0 \frac{I_{20,\eta_2}}{I_{20,0}} \quad \text{and} \quad S_1 = S_0 \frac{I_{20,\eta_1}}{I_{20,0}}
\]

where \( S_0 \) is the surface of the platinum wire electrode plated with copper and an initial cadmium layer.

RESULTS AND DISCUSSION

Typical polarization curves for cadmium deposition are shown in Fig. 1.

![Fig. 1. Polarization curves for the cathodic process of cadmium deposition from: 0.1 M CdSO\(_4\) + 0.5 M H\(_2\)SO\(_4\) (– – –), and from 0.1 M CdSO\(_4\) + 0.1 M (NH\(_4\))\(_2\)SO\(_4\) (– – –) solutions.](image)

It can be seen from Fig. 1 that diffusion control begins at considerably lower overpotentials in the sulfate than in the ammonium solution.
The determination of surface energy was performed as described earlier and the obtained results are presented in Tables I and II.

**TABLE I. Estimated values of the surface energy of the formation of a disperse cadmium electrodeposit from sulfate solution (0.1 M CdSO\(_4\) + 0.5 M H\(_2\)SO\(_4\)).**

<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>(I/t) A s</th>
<th>(\eta_2) mV</th>
<th>(\eta_1) mV</th>
<th>(S_2)/cm(^2)</th>
<th>(S_1)/cm(^2)</th>
<th>(\gamma)/J cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.1</td>
<td>95</td>
<td>75</td>
<td>2.25</td>
<td>1.29</td>
<td>375</td>
</tr>
<tr>
<td>2</td>
<td>32.6</td>
<td>105</td>
<td>75</td>
<td>3.09</td>
<td>1.27</td>
<td>537</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>100</td>
<td>80</td>
<td>1.06</td>
<td>0.71</td>
<td>431</td>
</tr>
<tr>
<td>4</td>
<td>9.5</td>
<td>100</td>
<td>80</td>
<td>1.23</td>
<td>0.91</td>
<td>601</td>
</tr>
<tr>
<td>5</td>
<td>9.0</td>
<td>100</td>
<td>80</td>
<td>1.48</td>
<td>1.12</td>
<td>510</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>100</td>
<td>60</td>
<td>1.15</td>
<td>0.62</td>
<td>446</td>
</tr>
</tbody>
</table>

**TABLE II. Estimated values of the surface energy of the formation of a disperse cadmium electrodeposit from ammonium solution (0.1 M CdSO\(_4\) + 0.1 M (NH\(_4\))_2SO\(_4\)).**

<table>
<thead>
<tr>
<th>No. of experiment</th>
<th>(I/t) A s</th>
<th>(\eta_2) mV</th>
<th>(\eta_1) mV</th>
<th>(S_2)/cm(^2)</th>
<th>(S_1)/cm(^2)</th>
<th>(\gamma)/J cm(^{-2})</th>
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<td>100</td>
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<td>0.52</td>
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<td>2</td>
<td>15.1</td>
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<td>130</td>
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<tr>
<td>3</td>
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<td>135</td>
<td>1.17</td>
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<tr>
<td>4</td>
<td>15.0</td>
<td>155</td>
<td>135</td>
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<td>0.66</td>
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<tr>
<td>5</td>
<td>14.5</td>
<td>155</td>
<td>135</td>
<td>0.95</td>
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<tr>
<td>6</td>
<td>19.0</td>
<td>155</td>
<td>135</td>
<td>1.08</td>
<td>0.90</td>
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</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>155</td>
<td>135</td>
<td>0.90</td>
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</tr>
<tr>
<td>8</td>
<td>25.8</td>
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<td>9</td>
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<td>135</td>
<td>1.16</td>
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<td>145</td>
<td>125</td>
<td>1.43</td>
<td>1.13</td>
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</tr>
</tbody>
</table>

It can be seen from Tables I and II that the surface energy determined in this way does depend on the composition of the solution. Hence, the measured surface energy is not the surface tension of solid cadmium but the surface energy of the formation of a disperse cadmium deposit, which includes all the energetic requirements for disperse cadmium electrodeposition. A more detailed analysis of this will be the subject of a following paper.

**Acknowledgements:** This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia under the research project “Electrochemical analysis and characterization of alloy composites and micro structured materials” (H1821).
ИЗВОД

ПОВРШИНСКА ЕНЕРГИЈА ЕЛЕКТРОХЕМИЈСКОГ ФОРМИРАЊА ДИСПЕРЗНОГ ТАЛОГА КАДМИЈУМА

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Површинска енергија електрохемијског формирања дисперзног талога кадмијума одређена је према раније описаној процедури. Показано је да површинска енергија у великој мери зависи од састава електролита из кога је формиран талог.

(Примљено 15. априла 2004)

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