JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 287–289

Electrodeposition of mercury from the $HgNO_3$-CH_3OH-H_2O system at low temperature

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Received 26 June 1980

Peculiar dendritic deposits of mercury were obtained galvanostatically from the mercurous nitrate–methanol–water system at −50° C. These deposits could not be maintained at a constant shape because, when the current was interrupted, they transformed and shrank immediately to a spherical shape with hydrogen evolution. It seems that when the electrical potential was removed, the mercury deposits liquefied and the hydrogen stored in them was released during the period of shrinking.

1. Introduction

As part of a series of investigations into the electrocrystallization of metals, the electrodeposition of mercury has been studied at low temperature. Several authors [1–3] have already reported on the conditions for dendritic deposition of iron, nickel and cobalt (the so-called inert metals) and their alloys; these are: high salt concentrations, high temperatures (near boiling point) and very high current densities. Chromium dendrites were obtained from CrO_3–H_2SO_4 aqueous solutions containing a small amount of dimethylsulphoxide [4]. On the other hand, level deposits of silver, zinc and manganese, which easily form well-defined dendrites under normal conditions, were obtained at lower temperature and current density [5, 6].

The work reported in the present paper relates to the electrodeposition of mercury at temperatures below its freezing point (−38.9° C). It was observed that mercury deposits in a liquid form near its freezing point. At a temperature around −50° C the deposits were bright and took a nodular or dendritic form, obviously not liquid.

2. Experimental

A methanol–water mixture (58:42 vol%) was used as the solvent as it does not solidify and its viscosity does not increase remarkably over a wide range of temperatures below the freezing point of mercury. The experimental apparatus is shown schematically in Fig. 1: 'a' is the electrolyte reservoir, through which the electrolyte was circulated to the electrolytic cell 'b'. Cooling was by air (−90 to −100° C). Fig. 2 shows the electrolytic cell consisting of a cylindrical Pt anode of 20 cm^2 area and a Pt cathode embedded in epoxy resin except for the top surface. The surface area of the cathode was 0.03 cm^2 and the current densities shown refer to this initial surface. Electrolysis was carried out at constant current density by a galvanostat. The electrolyte and the optimum

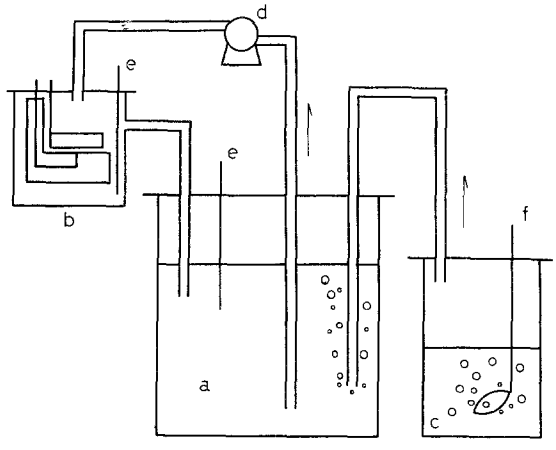

Fig. 1. Experimental apparatus. a, electrolyte reservoir; b, electrolytic cell; c, liquid air; d, centrifugal pump; e, thermometer; f, copper heat conductor.

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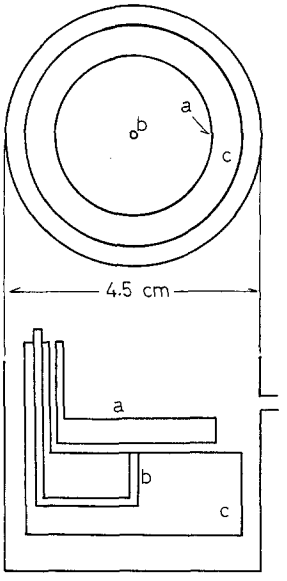

Fig. 2. Electrolytic cell. a, cylindrical Pt anode; b, Pt cathode; c, epoxy resin table.

operating conditions for dendritic deposits are as follows:

Solvent – methanol	58 vol%
– water	42 vol%
Conc. HNO_3	5 $cm^3 l^{-1}$
$HgNO_3 \cdot 2H_2O$	80 $g l^{-1}$
Temperature	−50° C
Cell voltage	25–30 V
D_k	12 A cm^{-2}
pH	0.4

3. Results and discussion

Nitric acid was added to improve the solubility of mercurous nitrate and the electrical conductivity of the solution. When the content of nitric acid was more than 7 vol%, mercury was electrodeposited with difficulty because of the preferential evolution of hydrogen. When the solvent contained 80 vol% or more of methanol, the solubility of mercurous nitrate became lower and, on cooling the electrolyte below −30° C, white precipitates, presumably mercurous nitrate, were formed. When the temperature was slightly lower than the freezing point of mercury, the deposits took on a spherical form that seemed to be liquid. Fig. 3 shows the deposits of mercury obtained at

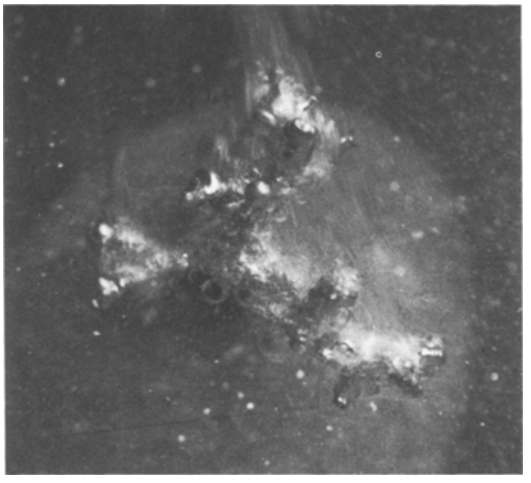

Fig. 3. Dendritic deposits of mercury on Pt obtained from the mercurous nitrate–methanol–water system at −50° C and 12 A cm^{-2}.

−50° C, which took an irregularly dendritic form with round edges.

Particularly interesting phenomena were observed in the morphologies of the deposits:

(a) The appearance of the macroscopic dendritic deposits was ill-defined and they had round edges.

(b) Bending of the stems and branches and a shape change of the deposits were observed during electrodeposition.

(c) The stems and branches of the dendritic deposits shrank slightly with a lowering of the cell voltage. When the current was cut off, the deposits transformed immediately to a spherical shape with the simultaneous evolution of gas.

The phenomena described above are shown in Fig. 4, which is a simplified sketch of the change in shape of the deposits. Fig. 4a shows a growing dendritic deposit with hydrogen evolution, Fig. 4b a slightly shrunken deposit, obtained by decreasing the current. Even when the current density was decreased to one tenth of that of Fig. 4a the deposit morphology was hardly changed and the evolution of gas ceased. Fig. 4c shows the spherical deposit after current interruption. Gas evolution again took place during the period of shrinkage from dendritic to spherical shape. The gas was identified as hydrogen by gas chromatographic analysis.

Though it cannot be imagined that the mercury deposits which looked dendritic in shape were

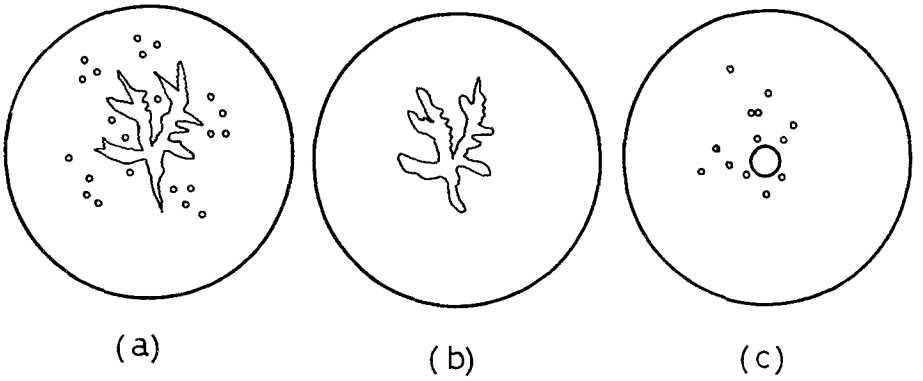

Fig. 4. Representation of the shape change of mercury deposit before and after current interruption. (a) a growing deposit with hydrogen evolution, at an initial current density of 12 A cm^{-2}; (b) a slightly shrunken deposit, obtained by decreasing the current density to about one tenth of that in (a); (c) a spherical solid deposit accompanied by hydrogen evolution immediately after current interruption.

liquid, they were not rigid since they could change shape. It was also found that they had an elasticity in an electric field, while the spherical deposits after current interruption became rigid. Therefore, it may be considered that the dendritic deposits are stable in the presence of an electrical potential and the change of the morphology by current interruption occurs through the liquefaction of dendritic deposits with simultaneous hydrogen evolution.

4. Conclusions

The following conclusions were obtained:

(a) The mercury deposits took a bright and irregular dendritic form at temperatures below $-50°$ C.

(b) The growing edges of the deposits were round and ill-defined, in contrast to the fine dendrites of silver, etc.

(c) The stems and branches of deposits bent slowly and positional changes occurred during electrodeposition.

(d) The dendritic deposits shrank slightly with decreasing current and gas evolution ceased.

(e) When the circuit was cut off, the deposits transformed immediately to become spherical with gas evolution.

(f) This gas was identified as hydrogen.

(g) The shrinkage and transformation occurred presumably through the liquefaction of the mercury deposits.

References

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