ELECTROREDUCTION OF CHROMIUM (III) - ACETATE COMPLEX TO METALLIC CHROMIUM ON THE COPPER ELECTRODE

I. DRELA, J. SZYNKARCZUK^{*}, J. KUBICKI

Institute of Inorganic Technology and Mineral Fertilizers, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

(Received 20 October 1987; in revised form 9 December 1987)

INTRODUCTION For the commercial purposes chromium is plated mostly from aqueous chromic acid baths. Because of problems including the technical difficulties (to low current efficiency, high cathode current densities, the relative toxity of hexavalent chromium), extensive work has been conducted in recent years [1-3] in order to develop trivalent chromium electrolytes. The purpose of this study is the investigation of the electrodeposition of metallic chromium from chromium (III) acetate. Such a study enables the determination of potentials for which the platingprocess can occur and, hence, may be useful for further, more detailed investigations.

EXPERIMENTAL Chromium acetate was prepared by reduction of CrO_3 in CH_3COOH (99.5 %) with H_2O_2 (30 %). The excess of hydrogen peroxide was destroyed by refluxing the solution. The chromium concentration was determined spectrophotometrically by oxidation of Cr (III) to Cr (VI) by ammonium persulfate in the presence of a trace amount of AgNO₃ as a catalyst. Ammonium acetate was synthesized from acetic acid and ammonium carbonate. It was recrystallized from water by the addition of methanol. All of the compounds used in synthesis were of $\rho\alpha$ grade.

Voltammetric experiments were performed with conventional threecompartment cells. Before each experiment copper was electrochemically deposited on the copper rod. The electrode was polished in the standard way [4]. The electrode area amounted to 0.06 cm². All potentials are quoted us a saturated calomel electrode. Dissolved oxygen was removed from the solution using purified argon bubbling for at least 20 min before each experiment.

RESULTS AND DISCUSSION The voltammetric behaviour of $[Cr(ac)_3]$ in the solution of CH_3COONH_4 as a supporting electrolyte is shown in Fig.1. Perchlorate acid was added just to fix the pH. The voltammetric curves obtained in the same conditions but at pH=3.5 and 4.0 were similar to those showed in Fig.1. One can notice that in the region -1.40 to -1.80 V the height of the wave decreases with the increase of complex concentration (except the first curve in Fig.1). After reaching the potential value +1.80 V the situation changes. The largest slope is





Fig.1. Voltammetric curves recorded in the 0.5 M CH_3COONH_4 , 0.3 M $HCIO_4$ (a supporting electrolyte) solutions with addition of chromium acetate of concentration: 1)0.0 M, 2) 0.005 M, 3) 0.010 M, 4) 0.025 M, 5) 0.050 M. The pH was adjusted to 4.5. Scan rate 0.5 V·s⁻¹.

Fig.2. The voltammogram of 0.050 M $[Cr(ac)_3]$ in a supporting electrolyte (0.5 M CH₃COONa and 0.4 M HClO₄). The pH was adjusted to 3.5. Scan rate 0.5 V·s⁻¹.

We were interested in the electrodeposition of metallic chromium from chromium (III) acetate in such conditions. However, a peak of the reduction process Cr^{+3}/Cr^{0} has not been observed. In order to check whether there is a trace of metallic chromium, controlled-potential electrolysis was performed. Then, time of dissolving metallic chromium in the 15 % solution of HCl was determined. The results obtained for different potentials are presented in Table 1.

The chromium coatings were obtained by electrolysis of the solution: $0,050 \text{ M} [Cr(ac)_3]$, $0.5 \text{ M} CH_3COONH_4$, $0.3 \text{ M} HClO_4$ (Fig.3).

Analogous experiments were carried out using sodium acetate as a supporting electrolyte. Recorded voltammograms at pH=3.5, 4.0 and 4.5 resembled those shown in Fig.1. But there was an exception. One can see an inflexion point at approximately -1.40 V. Above this potential it is possible to deposit chromium (see also Tab.1). In opposition to ammonium acetate all solutions based on sodium acetate showed poor plating abilities at pH=4.5. One can suppose that in this case the formation of polynuclear complexes takes place [5].

In order to get the chromium coating from the electrolyte presented in Fig.2, potential was fixed at -2.00 V and electrolysis lasted an hour. The surface of electrodeposited chromium is shown in Fig.4. Increasing the concentration of sodium acetate we obtained the best chromium coating ever received in our experiments (Fig.5).

chromium acetate.

Table 1.

Time of dissolving metallic chromium in the 15 % solution of HCl (time of H_2 bubbling in reaction: Cr + 2HCl \rightarrow CrCl₂+ H₂). Controlled-potential electrolysis lasted 10 min.

| ън | E/V | (se CH3COONH4) | t/s (se CH ₃ COONa) |
|-----|-------|----------------|-----------------------------------|
| 3.5 | 1.40 | - | ~ |
| | 1.425 | sb+) | sb |
| | 1.45 | sv++) | s▼ |
| | 1.60 | 3 | 5 |
| | 1.80 | 4 | 5 |
| | 2.00 | 5 | 4,5 |
| 4.5 | 1.40 | - | - |
| | 1.425 | sb | sb |
| | 1.45 | sv | sv |
| | 1.60 | 2,5 | sb |
| | 1.80 | 3.5 | - |
| | 2.00 | 3.5 | - |

sb⁺⁾ some bubbles sv several bubbles

se supporting electrolyte

It is not clear whether electroreduction of chromium (III) complexes to metallic chromium goes without intermediates [1]. Some workers suggest two step kinetics : Cr^{+3}/Cr^{+2} then Cr^{+2}/Cr^{0} [2]. Curves shown in Fig.1 and 2 have no peaks responsible for the reduction process Cr^{+3}/Cr^{+2} . There is only a wave from hydrogen-evolution reaction taking place together with reduction of Cr^{+3}/Cr^{0} . Probably the inflexion shown in Fig.2 is due to the electroreduction of the chromium (III) - acetic complex to metallic chromium. Therefore we suggest that this complex is reduced at once (without intermediate Cr^{+3}/Cr^{+2} process) to Cr^{0} .

There are a few known electrolytes, based on Cr^{+3} salts [1-3] from which chromium can be electrodeposited. We believe that chromium acetate can be considered as a candidate for application.



Fig.3. Surface (seen) of chromium deposited from the solution: 0.5 M CH_3COONH_4 , 0.3 M HClO₄ and 0.050 M [Cr(ac)₃]. Controlled-potential electrolysis was performed during an hour, E = -2.20 V, pH = 4.5.



Fig.4. Surface (sem) of chromium deposited from the solution: 0.5 M CH_3COONa , 0.4 M $HClo_4$, 0.050 M $[Cr(ac)_3]$. Controlled-potential electrolysis was performed during an hour, E = -2.00 V, pH = 3.5.



Fig.5. Surface (sem) of chromium deposited from the solution: 1.0 M CH₃COONa, 0.4 M $HC1O_4$, 0.050 M [Cr(ac)₃]. Controlled-~potential electrolysis was performed during an hour, E = -1.80 V, pH = 3.9.

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