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# Electrodeposition of chromium from Cr (III) electrolytes in the presence of formic acid

I. DRELA, J. SZYNKARCZUK*, J. KUBICKI

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

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Chromium coatings deposited from sulphate, chloride and perchlorate electrolytes based on the $[Cr(H_2O)_4(HCOO)]^{2+}$ complex ion were investigated. The current efficiency reached 30% in the case of chloride electrolyte for various current densities in the range 4–10 A dm$^{-2}$ depending on pH. Such a large current efficiency is due to the catalytic effect of the chloride ions on the electroreduction of the chromium complex to metallic chromium. Deposition of chromium from sulphate electrolyte took place with a current efficiency of 16% which rose for higher pH and lower current densities. Semi-bright and bright coatings with thickness of approximately 10 $\mu$m of good adhesion to a copper electrode were deposited from chloride and sulphate electrolytes.

## 1. Introduction

In recent years [1–9] considerable development of commercially accessible trivalent chromium electrolytes based on organic chromium (III) complexes has been achieved. A few papers [6–8] have been devoted to the problem of metallic chromium deposition from electrolytes containing chromium (III) and formic acid. It has been found [4, 5] that sulphur containing compounds accelerate chromium deposition. The catalytic function of these complexes facilitates a reaction pathway with a lower transition state energy than in the absence of catalyst [4].

The aim of the present work was to investigate the influence of supporting electrolytes ($Na_2SO_4$, KCl, $NaClO_4$), solution pH, the presence of trace amounts of thiourea and the current density and electrolysis time on the process of chromium deposition. The current efficiency and the quality of the coatings were also investigated.

## 2. Experimental

Three kinds of electrolyte were prepared according to following compositions: 0.25 M $Cr_2(SO_4)_3 \cdot 18H_2O$ and 1 M $Na_2SO_4 \cdot 10H_2O$; 0.5 M $CrCl_3 \cdot 6H_2O$ and 1.5 M KCl; 0.3 M $Cr(ClO_4)_3$ and 1 M $NaClO_4$; $H_3BO_3$ was added (0.5 M) in order to improve the quality of the coatings. The molar ratio [Cr(III)]: [HCOOH] was kept at 1 : 2 for each solution. Under these conditions the following chromium complexes exist: $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_4(HCOO)]^{2+}$ and $[Cr(H_2O)_{6-x}Cl_x]^{3-x}$ [10–12] in chloride electrolyte. A few experiments with sulphate electrolyte were carried out in the presence of a trace amount of thiourea (20 ppm). In perchlorate electrolyte thiourea was present in all solutions. All solutions were kept at ambient temperature for 30 days to attain equilibrium of complex formation. During this time the pH was adjusted by adding sodium hydroxide or an acid ($H_2SO_4$, $HClO_4$, HCl). All compounds used were of pa grade; water was doubly distilled.

The current efficiency of chromium deposition was investigated in a three-compound cell. The cathode compartment of the cell was separated by two G4 ceramic sinters. A copper cathode (area: 2 cm$^2$) and two identical platinum anodes (area: 4 cm$^2$) were employed. The copper electrode was plated on both sides. Its surface was polished with an abrasive paper (no. 800 and no. 1000), etched in $HNO_3$ (30%), cleaned with water and dried with warm air. The amount of chromium deposited was determined by weighing. The electrolyte was stirred by a magnetic stirrer and temperature was kept constant (20° C) using a thermostat.

The values of potential quoted in this paper are referred to the saturated calomel electrode (SCE).

## 3. Results and discussion

### 3.1 *Sulphate electrolyte*

The current efficiency (*CE*) of chromium plating versus cathodic current density (*CD*) for different values of pH are presented in Fig. 1. The optimum *CD* lies in the range 2.5–3.7 A dm$^{-2}$. *CE* decreases with increasing pH. Chromium coatings could not be obtained for current densities below 2 A dm$^{-2}$ independently of pH.

The results presented in Fig. 2 indicate that the rate of deposition of chromium decreases with deposition time. This effect can be partially explained by the

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* Author to whom correspondence should be addressed.

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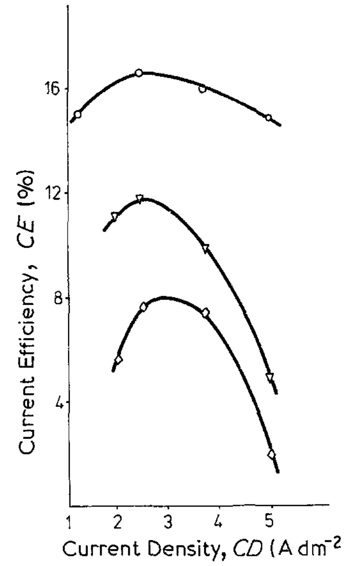

Fig. 1. Current efficiency (*CE*) of chromium plating as a function of current density (*CD*) for solutions containing: 0.25 M $Cr_2(SO_4)_3 \cdot 18H_2O$, 0.5 M HCOOH, 1 M $Na_2SO_4$, 0.5 M $H_3BO_3$ for different pH values. Electrolysis time, $T = 5$ min. ○, pH = 3.5; ▿, pH = 4.0; ◇, pH = 4.5.

exhaustion of the active form of the discharged complex from the bath.

The chromium plating efficiency doubles in the presence of a trace amount (20 ppm) of thiourea (compare the curves obtained for solution of pH = 4.5 in Fig. 2). This is a remarkably strong effect especially at the higher pH values in sulphate electrolytes and at low current densities.

An SEM micrograph showing the surface of chromium deposited from sulphate electrolyte is presented in Fig. 3a.

### 3.2. *Chloride electrolyte*

Chloride electrolyte behaves quite differently from sulphate. In this case thiourea does not enhance the current efficiency.

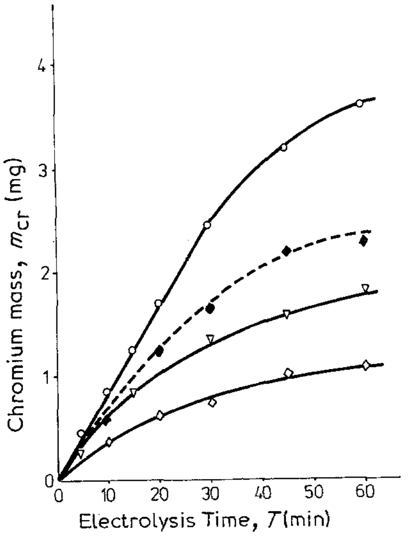

Fig. 2. Chromium mass ($m_{Cr}$) as a function of electrolysis time (*T*) for solutions with various pH, containing: 0.25 M $Cr_2(SO_4)_3 \cdot 18H_2O$, 0.5 M HCOOH, 1 M $Na_2SO_4$, 0.25 M $H_3BO_3$. Current density $CD = 2.5\,\mathrm{A\,dm^{-2}}$. ○, pH = 3.5; ▿, pH = 4.0; ◇, pH = 4.5; ◆, pH = 4.5 with 20 ppm thiourea.

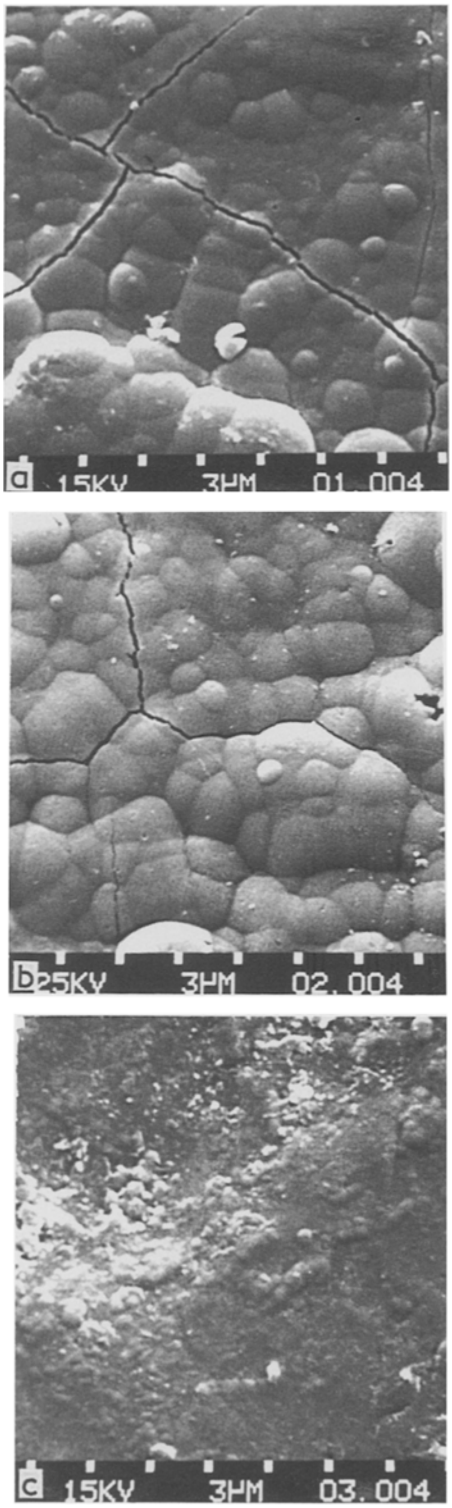

Fig. 3. Surface of chromium (SEM) deposited from: (a) sulphate electrolyte, (b) chloride electrolyte, (c) perchlorate electrolyte.

Chromium plating efficiency as a function of current density (*CD*) for different pH is shown in Fig. 4. Coatings useful from a technical point of view can be obtained within a pH range 2.5–3.5. In chloride solutions the potential for chromium deposition moves towards more negative values with decreasing pH and depends on cathodic current density. At higher pH the deposited chromium is dark and loses its adherence. Chromium cannot be deposited below a limiting value of *CD*. Chromium mass ($m_{Cr}$) as a function of electrolysis time (*T*) is presented in Fig. 5. There is a

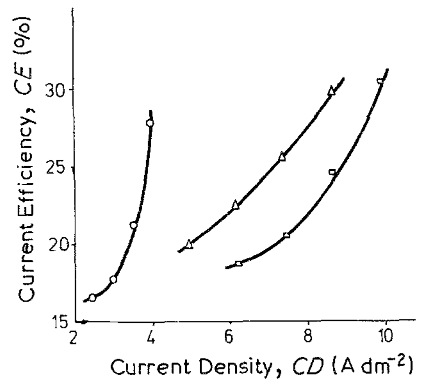

Fig. 4. Chromium plating efficiency (*CE*) as a function of current density (*CD*) for solutions containing: 0.5 M $CrCl_3 \cdot 6H_2O$, 1 M HCOOH, 1.5 M KCl, 0.5 M $H_3BO_3$, for different pH values. Electrolysis time $T$ = 5 min. □, pH = 2.5; △, pH = 3.0, ○, pH = 3.5.

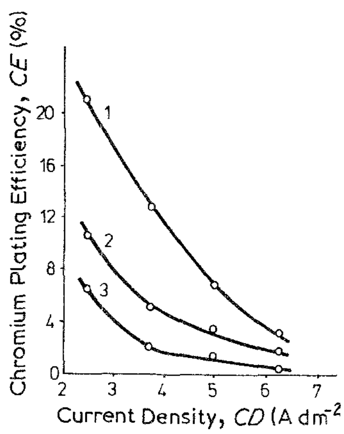

Fig. 6. Chromium plating efficiency (*CE*) as a function of current density (*CD*) for solutions containing: 0.3 M $Cr(ClO_4)_3$, 0.6 M HCOOH, 0.5 M $H_3BO_3$, 1 M $NaClO_4$, 20 ppm thiourea, pH = 3.0 for various electrolysis times: 1, $T$ = 1 min; 2, $T$ = 2 min; 3, $T$ = 3 min.

linear relationship between $m_{Cr}$ per unit time and electrolysis time (pH = 3.0, $CD = 6.25\,A\,dm^{-2}$, $T < 30$ min). Then the rate of chromium plating decreases rapidly and after 45 min of electrolysis no mass gain is observable.

Chloride electrolyte behaves slightly differently at lower pH. Chromium mass gain is considerable during the first 10 min of electrolysis, then is stabilizes, but at the lower level (pH = 2.5, $CD = 6.25\,A\,dm^{-2}$). Similar behaviour can be observed for electrolyte at pH = 3.5 but with $CD = 2.5\,A\,dm^{-2}$. Therefore, in chloride electrolyte the concentration of the active forms of $[Cr(H_2O)_4(HCOO)]^{2+}$, $[Cr(H_2O)_{6-x}Cl_x]^{3-x}$, and mixed complexes, have been reduced for higher current density and higher pH solutions.

An SEM micrograph showing the surface of chromium deposited from chloride electrolyte is presented in Fig. 3b.

The maximum current efficiency of chromium deposition was 30%, however, a few authors obtained higher values, up to 50%, but in non-aqueous [13] or water–dimethylformamide baths [14]. Data [1] obtained an efficiency of 14% in aqueous solutions.

### 3.3. *Perchlorate electrolyte*

To investigate the influence of chloride and sulphate ions on the electroreduction of chromium complexes, comparative measurements were carried out using a perchlorate electrolyte of similar composition. Since, otherwise it was impossible to deposit satisfactory chromium coatings a trace amount (20 ppm) of thiourea was added to each solution. The current efficiency (Fig. 6) and the rate of mass increase (Fig. 7) decrease with increase of current density and electrolysis time. Compact chromium coatings were obtained from perchlorate electrolyte only at pH = 3.0. These were mostly grey and dull (Fig. 3c), contrary to the coatings deposited from sulphate and chloride electrolytes which gave semi-bright and light grey deposits.

## 4. Conclusion

A comparison of the three electrolytes used for chromium plating and based on the $[Cr(H_2O)_4(HCOO)]^{2+}$ complex has been presented. The best quality chromium coatings were obtained from chloride electrolytes. Current efficiency was a function of current density and the pH. Its maximum value was as high as 30%.

Semi-bright and bright coatings were obtained from sulphate electrolytes with current efficiencies as high as 16%. Chromium coatings deposited from sulphate

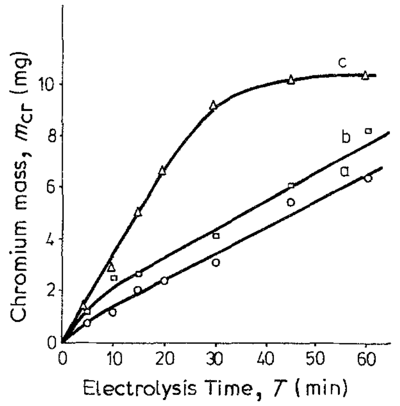

Fig. 5. Chromium mass ($m_{Cr}$) as a function of electrolysis time ($T$) for solutions of different pH, containing: 0.5 M $CrCl_3 \cdot 6H_2O$, 1 M HCOOH, 1.5 M KCl, 0.5 M $H_3BO_3$. (a) $CD = 3.5\,A\,dm^{-2}$; (b, c) $CD = 6.25\,A\,dm^{-2}$; □, pH = 2.5; △, pH = 3.0; ○, pH = 3.5.

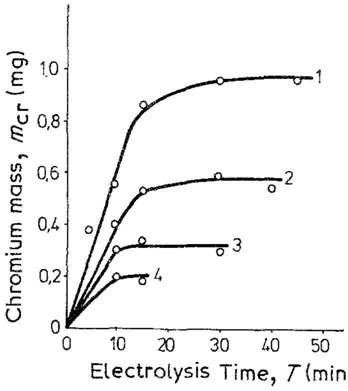

Fig. 7. Chromium mass ($m_{Cr}$) as a function of electrolysis time ($T$) for solutions of different current densities, containing: 0.3 M $Cr(ClO_4)_3$, 0.6 M HCOOH, 0.5 M $H_3BO_3$, 1 M $NaClO_4$, 20 ppm thiourea, pH = 3.0. (1) $2.5\,A\,dm^{-2}$; (2) $3.75\,A\,dm^{-2}$; (3) $5.0\,A\,dm^{-2}$; (4) $6.25\,A\,dm^{-2}$.

electrolyte feature high cracking frequency. Coatings obtained from chloride bath have lower frequency of microcracks whereas those deposited from perchlorate electrolyte are crack-free. A trace amount of thiourea decreased the chromium plating efficiency for solutions of higher pH and for lower current density. The current efficiency values obtained in chloride, sulphate and perchlorate electrolytes indicate that the largest catalytic effect on the electroreduction of chromium complex to metallic chromium occurs in the presence of chloride ions. Sulphates are also able to catalyse this process, but with a lower rate constant. The decrease of chromium plating efficiency during long-time electrolysis is explained by the exhaustion of the active chromium complexes in the solutions.

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