

# *Electropolishing of chromium in phosphoric acid-sulphuric acid electrolytes*

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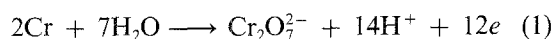
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The anodic dissolution of chromium in phosphoric acid-sulphuric acid electropolishing electrolytes has been investigated using a rotating disc electrode. The influence of electrolyte composition on mass transport and the resulting surface finish has been investigated. It was found that electropolishing of chromium occurs in the transpassive potential region under mass transport control. The transport limiting species is the anodically generated hexavalent chromium ion. The rate of nucleation of the anodic film present is potential dependent, and film instabilities occur in a certain potential region of the limiting current plateau.

## 1. Introduction

Electropolishing of stainless steels is widely practised in industry but little mechanistic information on the process is available. Commonly used industrial electropolishing electrolytes for stainless steels are based on the system phosphoric acid-sulphuric acid-water, the phosphoric and sulphuric acid concentration typically being 40-65% and 15-45%, respectively [1-3]. In the present study the anodic behaviour of chromium in  $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$  is investigated as a first step towards a better understanding of the mechanism of electropolishing of chromium-based alloys.

The kinetics of transpassive dissolution of chromium in sulphuric acid electrolytes has been studied by several authors who found Tafel behaviour and a dependence of the dissolution rate on pH [4-6]. Under these conditions chromium goes into solution in the hexavalent state, according to



The electropolishing mechanism of chromium has not been investigated to date, but several electropolishing electrolytes and corresponding electrical conditions are described in the literature [7-9]. McTegart [7] describes a solution containing 50 cm<sup>3</sup> perchloric acid and 1000 cm<sup>3</sup>

acetic acid at a current density of 15-20 A cm<sup>-2</sup> and a temperature of 20-30°C. According to Grilichjes [8] chromium can be polished in phosphoric acid at concentrations exceeding 30 wt %. An improvement is obtained by adding sulphuric acid, glycerol or citric acid to the solution. Excellent results are reported for an electrolyte containing 850 g l<sup>-1</sup>  $\text{H}_3\text{PO}_4$ , 180 g l<sup>-1</sup>  $\text{H}_2\text{SO}_4$  and 10 g l<sup>-1</sup> glycerol at a current density of 20-30 A cm<sup>-2</sup> and a temperature of 16-20°C.

It is well known that mass transport plays an important role in the electropolishing of copper and nickel [10-13]. Investigations on the mechanism of electropolishing, therefore, must be carried out under controlled mass transport conditions. In the present study a rotating disc electrode was employed for that purpose. The influence of electrolyte composition ( $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ ) on polarization behaviour was investigated and the resulting surfaces were observed by optical and scanning electron microscopy. In some cases Auger electron spectroscopy was employed for the characterization of surface films.

## 2. Experimental details

Rotating disc electrodes of 3.6 mm diameter (area 0.1 cm<sup>2</sup>) were fabricated from pure chromium (analysis, wt %: Mn, 0.001; Si, 0.001;

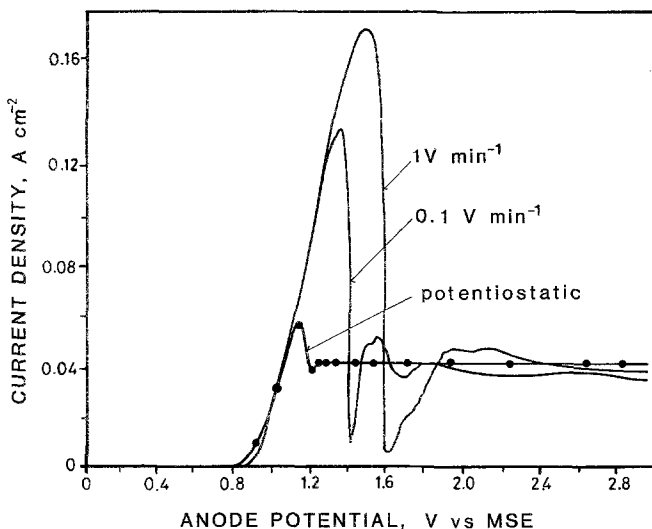


Fig. 1. Potentiodynamic and potentiostatic current-voltage curves of chromium in 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at 20°C and 400 r.p.m.

O, 0.210, present at oxide inclusions) obtained from Materials Research, Toulouse, France. A saturated mercurous sulphate electrode (MSE) was used as reference. The counter electrode was a platinum wire separated from the anode compartment by a glass frit. The anode compartment volume was 700  $\text{cm}^3$ . The temperature was maintained by a thermostat at 6, 30 or 70°C. The rotation rate was varied from 100 to 4900 r.p.m. The Luggin capillary leading to the reference electrode was placed at  $\sim 1$  cm below the disc electrode. No ohmic potential drop correction was performed, the correction being small under the present experimental conditions. A potentiostat (Amel 555/SU) was used as power supply; current and potential were recorded on an X-Y plotter.

Before each experiment the anode was mechanically polished on 240 and 600 paper then with diamond powder to a finish of 1  $\mu\text{m}$ . It was rinsed with ethanol and doubly distilled water, then dried with warm air. Before starting a polarization experiment the electrode was left in the electrolyte for 10 min. Electrolytes were prepared from doubly distilled water and chemically pure reagents (sulphuric acid 96% p.a. Merck, phosphoric acid 85% p.a. Merck, chromic acid p.a. Merck). Unless otherwise stated the compositions in the present paper are given in wt %.

### 3. Results

#### 3.1. Potentiodynamic experiments

Fig. 1 shows the influence of scan rate on the shape of the current-voltage curves measured in a solution of 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at a rotation rate of 400 r.p.m. at 20°C. The anodic current increases at potentials  $> 850$  mV (all values are given with respect to the saturated MSE) corresponding to the transpassive potential region. A current maximum is observed, but at sufficiently high potential a plateau current independent of scan rate is established. Its value corresponds to that measured in potentiostatic experiments. The influence of temperature and of rotation rate on the current-voltage behaviour was investigated for a constant scan rate of  $0.1 \text{ V s}^{-1}$ . Fig. 2 shows the influence of rotation rate at 20°C. With increasing rotation rate the values of the current at the maximum and on the plateau both increase, and current oscillations are observed in the plateau region. The variation of the plateau current density with rotation rate is presented in Fig. 3 for the three temperatures (6, 20 and 70°C). The presentation is based on the Frumkin-Tedoradse [14] equation:

$$\frac{1}{i_1} = \frac{1}{i_0} + \frac{1}{B\omega^2} \quad (2)$$

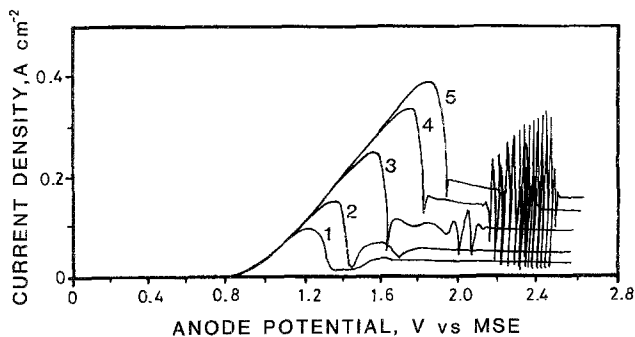


Fig. 2. Potentiodynamic current-voltage curves at different rotation rate. Scan rate,  $0.1 \text{ V min}^{-1}$ ;  $T = 20^\circ \text{C}$ . Electrolyte: 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$ .

Here  $i_l$  is the measured plateau current density,  $i_\infty$  is the current density at infinite rotation rate,  $B$  is a constant given by

$$B = \frac{nFD^{3/2}\Delta c}{1.61\nu^{1/2}} \quad (3)$$

$\omega$  is the rotation rate in  $\text{rad s}^{-1}$ ,  $\nu$  is the kinematic viscosity,  $D$  is the diffusion coefficient and  $\Delta c$  is the concentration difference between surface and bulk of the diffusion limiting species. For all three temperatures a linear dependency of the reciprocal of the plateau current density on the reciprocal of the square root of the rotation rate is observed, with projections of the straight lines passing through the origin. The reaction rate at the plateau current therefore is mass transport controlled.

The shape of the current-potential curves and

the value of the plateau current are strongly affected by the sulphuric acid content of the electrolyte. This is demonstrated by Fig. 4, which shows results obtained in electrolytes of constant water content but varying  $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$  ratio under otherwise identical experimental conditions. In a sulphuric acid-free electrolyte a plateau current is reached without a preceding current maximum. Increasing the sulphuric acid content leads to increasingly pronounced current maxima and a depression of the value of the plateau current. The variation of the plateau current density with the sulphuric acid and the phosphoric acid content is presented in Fig. 5. Above  $\sim 20\%$   $\text{H}_2\text{SO}_4$  the current attains a limiting value which stays the same up to at least 65%  $\text{H}_2\text{SO}_4$ . In all cases the reaction is mass transport controlled, a plot of  $i/i_l$  versus

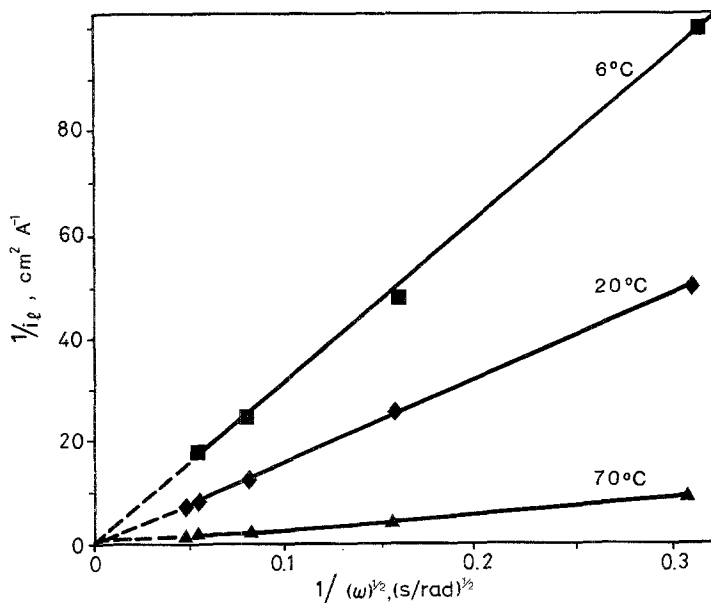


Fig. 3. Reciprocal of limiting current as a function of reciprocal of square root of rotation rate for chromium dissolution in 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at different temperatures.

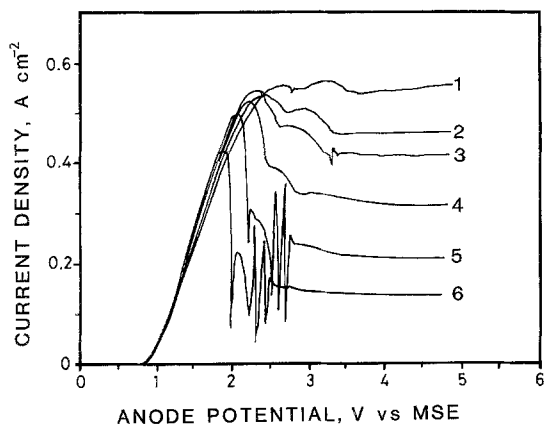


Fig. 4. Potentiodynamic current-voltage curves for different ratios of  $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$  in the presence of 15%  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$  and 3600 r.p.m. 1, 85%  $\text{H}_3\text{PO}_4$ ; 2, 81%  $\text{H}_3\text{PO}_4$ , 4%  $\text{H}_2\text{SO}_4$ ; 3, 78%  $\text{H}_3\text{PO}_4$ , 7%  $\text{H}_2\text{SO}_4$ ; 4, 75%  $\text{H}_3\text{PO}_4$ , 10%  $\text{H}_2\text{SO}_4$ ; 5, 69%  $\text{H}_3\text{PO}_4$ , 16%  $\text{H}_2\text{SO}_4$ ; 6, 63%  $\text{H}_3\text{PO}_4$ , 22%  $\text{H}_2\text{SO}_4$ .

$1/\omega^{\frac{1}{2}}$  yielding straight lines passing through zero.

A series of experiments was performed in a phosphorous acid-free solution of 85%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$ . The polarization curves (Fig. 6) exhibit a quite different behaviour from those measured in the presence of phosphoric acid; the plateau currents are less well defined and almost independent of rotation rate. At potentials above 4 V an abrupt current increase occurs, accompanied by gas evolution on the anode. The data show that the anodic reaction kinetics are different in phosphoric acid than in sulphuric acid.

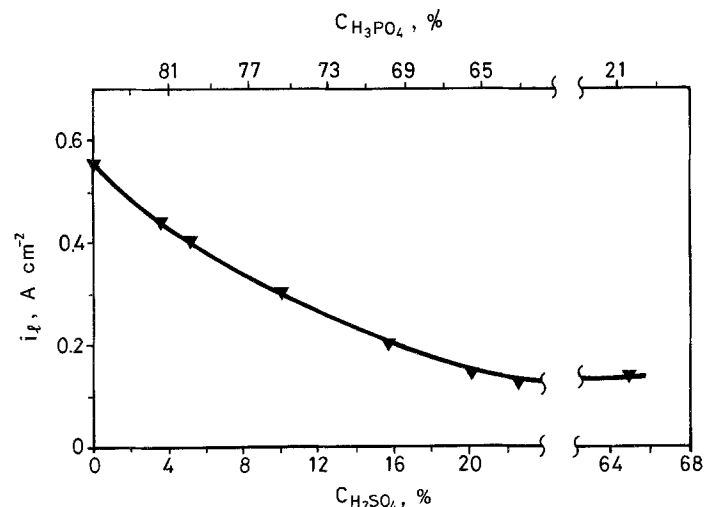


Fig. 5. Limiting current density as a function of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  content in electrolytes containing 15%  $\text{H}_2\text{O}$  at  $20^\circ\text{C}$  and 3600 r.p.m.

To obtain further information on the nature of the anodic reactions and the diffusion limiting species experiments were performed in phosphoric acid solutions saturated with chromic acid. Results for  $70^\circ$  corresponding to a solution composition of 71%  $\text{H}_3\text{PO}_4$ , 12.5%  $\text{H}_2\text{O}$  and 16.5%  $\text{CrO}_3$  are shown in Fig. 7. The presence of  $\text{CrO}_3$  decreases the plateau current density to very low values. Maxima are observed which are absent in phosphoric acid solutions that do not contain chromic acid (cf. Fig. 4). The shape of the curves in Fig. 7 suggests that the reactions responsible for the suppression of the diffusion-limited plateau current proceed slowly. Potentiostatic experiments confirmed this. For example, when a constant potential of 1 V was imposed the anodic current dropped over a period of 60 min to a very low value.

### 3.2. Surface morphology

Dissolution experiments were carried out at constant potential in 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at 3600 r.p.m. Current transients measured at  $20^\circ\text{C}$  are shown in Fig. 8. At potentials negative to the limiting current plateau region a steady state was rapidly reached, as illustrated by the transient for 1.2 V. At the limiting current the time to reach steady state depended on applied potential. For example at 1.4 V it took 80 min, at 1.6 V it took 20 min and at 1.8 V it took 1 min to reach a steady-state current. At 2.2 V, current oscillations occurred; at

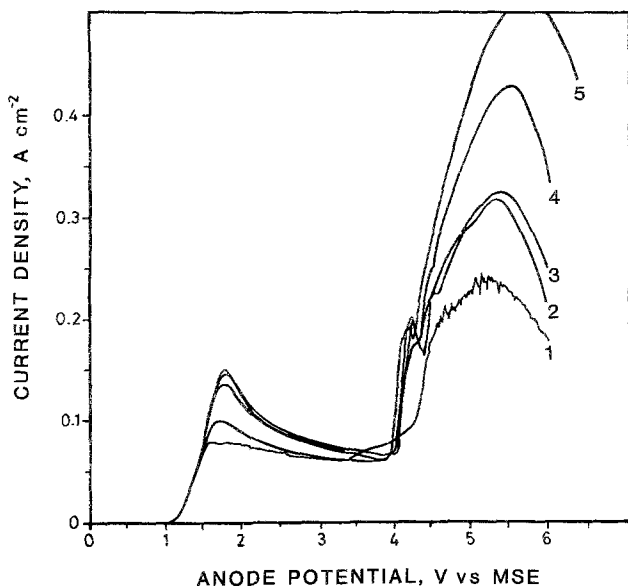


Fig. 6. Potentiodynamic current-voltage curves in 85%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at different rotation rates.  $T = 20^\circ\text{C}$ ; scan rate,  $0.1\text{ V min}^{-1}$ .

2.4 V and higher potentials, steady-state currents were reached in a matter of seconds. The behaviour suggests formation of anodic surface films with a potential-dependent rate of nucleation. Scanning electron micrographs of surfaces after dissolution corresponding to a charge of  $80\text{ C cm}^{-2}$  are shown in Fig. 9. The surface resulting from dissolution at 1.6 V (Fig. 9a) exhibits crystallographic etching. Dissolution time corresponds to the non-steady-state region of the current transient where the anodic film is not yet formed. The same surface morphology was observed for dissolution at potentials nega-

tive to the limiting current region. The surface resulting from dissolution at 2.2 V (Fig. 9b) where current oscillations occurred exhibits microroughness independent of crystallographic structure. The surface resulting from dissolution at 2.4 V (Fig. 9c) is polished. The same type of surface structure was observed at 1.8 V. It is typical for dissolution under steady-state conditions at the limiting current. Non-metallic inclusions are visible on all surfaces. They were identified by electron microprobe analysis on chromium oxides and chromium carbides, the latter being present in smaller quantities.

At  $70^\circ\text{C}$ , steady state was reached more rapidly. Current oscillations were observed at a potential of 2 V and to a lesser extent at 2.2 and 2.4 V. The resulting surface morphology qualitatively corresponded to that observed for comparable conditions at  $20^\circ\text{C}$ , with the exception of the surface resulting from dissolution at 2.4 V which exhibited a regular non-crystallographic microwaviness (Fig. 10). The electrochemical mechanism leading to this particular structure is not known, but must be related to the unstable behaviour of the anodic film in this potential range.

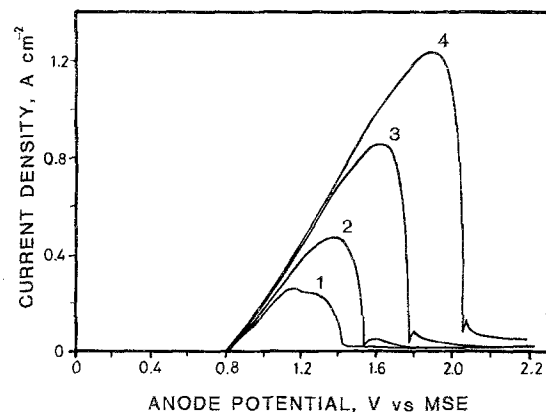


Fig. 7. Potentiodynamic current-voltage curves in 71%  $\text{H}_3\text{PO}_4$ , 12.5%  $\text{H}_2\text{O}$  and 16.5%  $\text{CrO}_3$  at different rotation rates.  $T = 70^\circ\text{C}$ .

### 3.3. Dissolution stoichiometry

The apparent valence of dissolution,  $n_{\text{ap}}$ , was

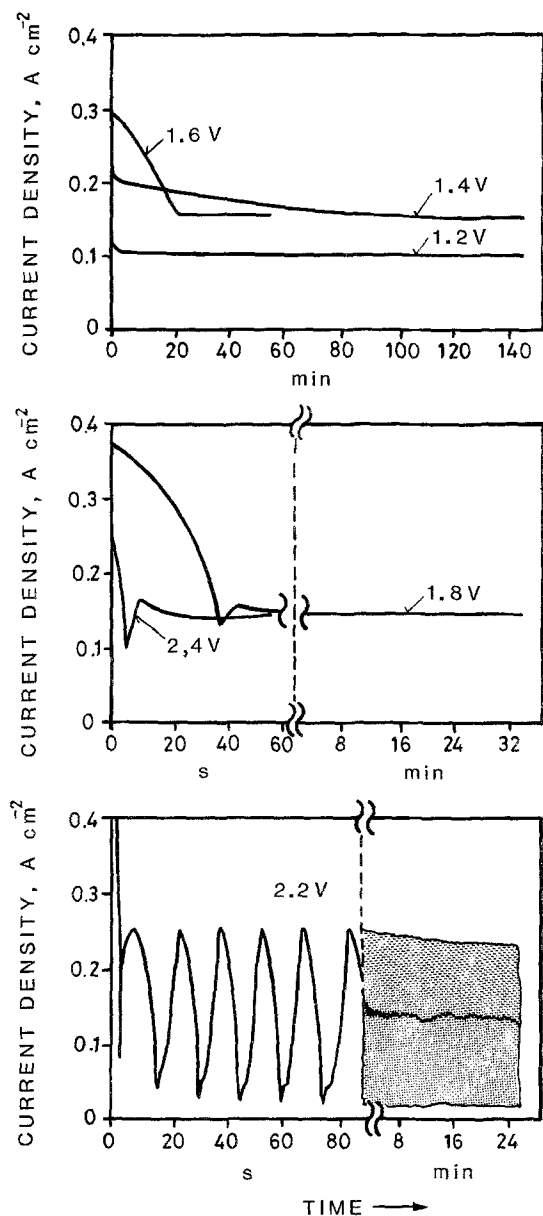


Fig. 8. Current density as a function of time at different applied potentials in 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  at 3600 r.p.m. and 20°C.

determined by weight loss measurements. The apparent valence of dissolution is defined by

$$n_{\text{ap}} = \frac{QA}{mF} \quad (4)$$

where  $Q$  is the charge density,  $m$  the dissolved mass (moles),  $A$  the surface area and  $F$  the Faraday constant. Results are given in Table 1.

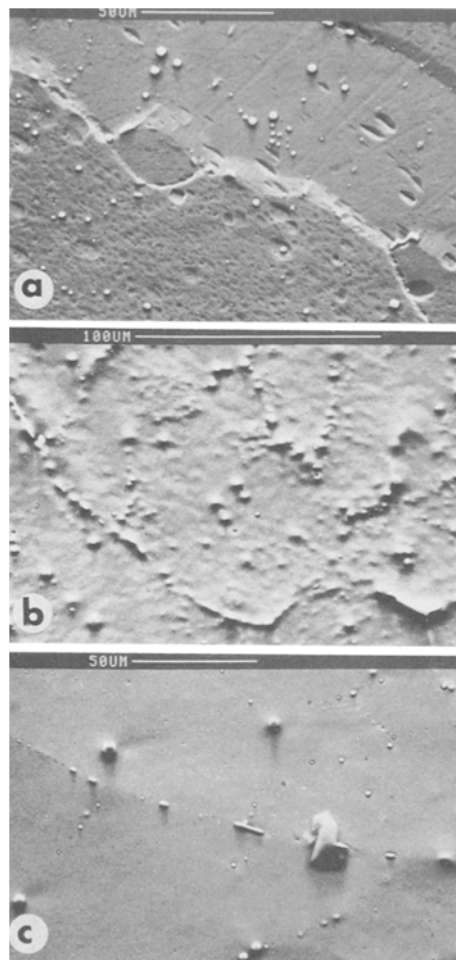


Fig. 9. Scanning electron micrographs of surfaces resulting from dissolution at constant potential in 65%  $\text{H}_3\text{PO}_4$  and 15%  $\text{H}_2\text{O}$  at 3600 r.p.m. and 20°C. (a) 1.6 V; (b) 2.2 V; (c) 2.4 V.

They confirm that under the present experimental conditions chromium goes into solution in the hexavalent state. Slight but systematic deviations from the theoretical value of  $n = 6$  are attributed to the behaviour of inclusions, but this aspect was not investigated further.

#### 3.4. Auger electron spectroscopy

A few surfaces were investigated by Auger electron spectroscopy (AES) depth profiling using a Physical Electronics Type 550/590A apparatus with differentially pumped ion guns. For this purpose dissolution was carried out at constant

Table 1. Apparent valence of dissolution for chromium at 20°C, 3600 r.p.m.

Electrolyte	Applied potential (V vs MSE)	$n_{ap}$
85% H <sub>3</sub> PO <sub>4</sub>	1.8	5.91
15% H <sub>2</sub> O	2.0	5.91
	4.0	6.00
65% H <sub>3</sub> PO <sub>4</sub>	1.2	5.87
20% H <sub>2</sub> SO <sub>4</sub>	1.6	6.00
15% H <sub>2</sub> O	1.8	6.04
	2.2	6.10
	2.6	6.13

potential in 85% H<sub>3</sub>PO<sub>4</sub>, 15% H<sub>2</sub>O and in 65% H<sub>3</sub>PO<sub>4</sub>, 20% H<sub>2</sub>SO<sub>4</sub>, 15% H<sub>2</sub>O. To obtain qualitative information on the influence of dissolution conditions on surface composition depth profiles measured on anodically polarized samples were compared to that of a standard consisting of a chromium electrode immersed in open circuit for 15 min in the 65% H<sub>3</sub>PO<sub>4</sub>, 20% H<sub>2</sub>SO<sub>4</sub> and 15% H<sub>2</sub>O electrolyte at 20°C at a rotation rate of 400 r.p.m. The AES depth profile of the standard is shown in Fig. 11a. The sputter rate of Ta<sub>2</sub>O<sub>5</sub> under the applied conditions is 0.8 nm min<sup>-1</sup>. The profile shows a rapidly disappearing signal of adsorbed carbon introduced during the cleaning and transfer procedure. An oxide film of the order of 1–2 nm is present. No sulphur or phosphorus are observed in the film. Electrodes polarized anodically in the 85% H<sub>3</sub>PO<sub>4</sub> and 15% H<sub>2</sub>O electrolyte exhibited

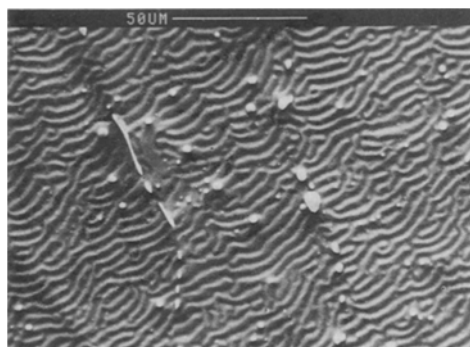


Fig. 10. Scanning electron micrograph of surface resulting from dissolution at constant potential of 2.4 V in 65% H<sub>3</sub>PO<sub>4</sub>, 20% H<sub>2</sub>SO<sub>4</sub> and 15% H<sub>2</sub>O at 3600 r.p.m. and 70°C. Charge = 80 C cm<sup>-2</sup>.

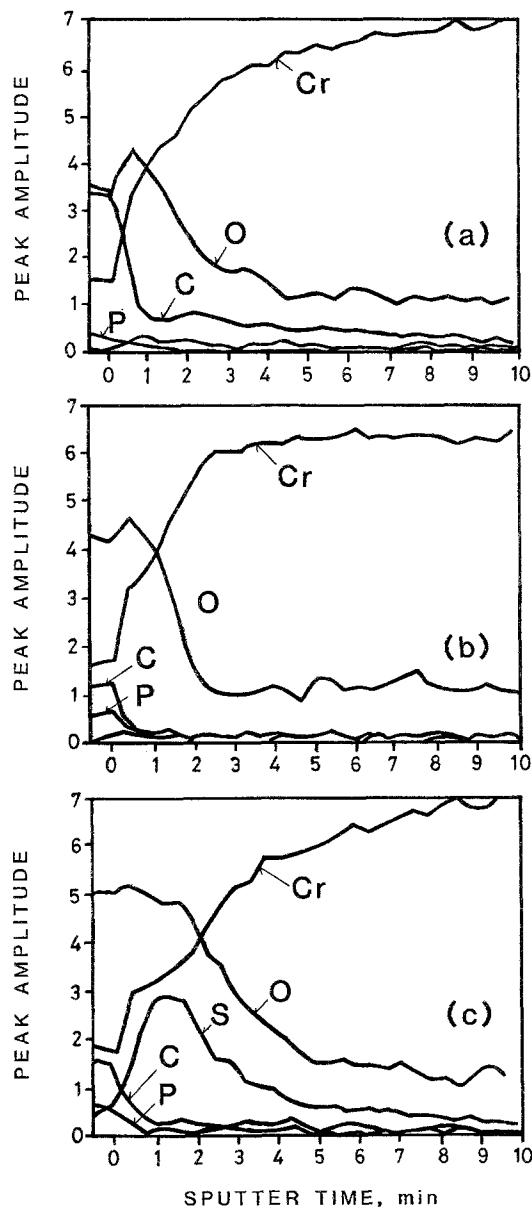


Fig. 11. Auger peak amplitudes of Cr, O, C, P and S (arbitrary units) as a function of sputter time. (a) Standard; (b) polarized at 1.8 V; (c) polarized at 2.6 V. Electrolyte: 65% H<sub>3</sub>PO<sub>4</sub>, 20% H<sub>2</sub>SO<sub>4</sub> and 15% H<sub>2</sub>O at 20°C and 3600 r.p.m. Charge = 80 C cm<sup>-2</sup>.

identical profiles to the standard. On the other hand, the profiles measured on samples polarized in the 65% H<sub>3</sub>PO<sub>4</sub>, 20% H<sub>2</sub>SO<sub>4</sub> and 15% H<sub>2</sub>O electrolyte showed a distinct sulphur signal at applied potentials positive to the region of current oscillations. At lower potentials no

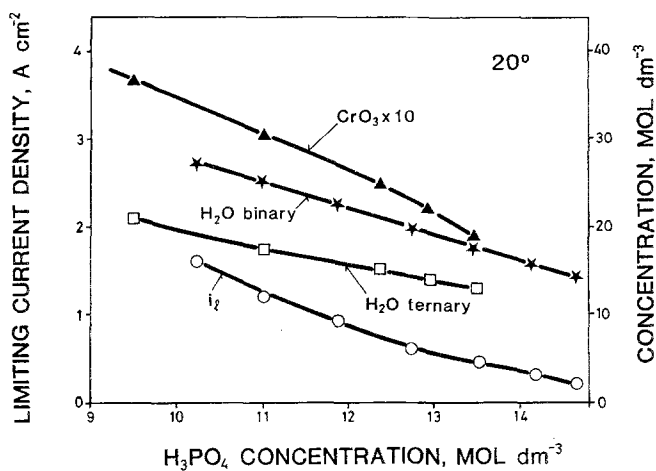


Fig. 12. Solubility of  $\text{CrO}_3$  in  $\text{H}_3\text{PO}_4$  of varying  $\text{H}_2\text{O}$  concentrations and limiting currents,  $i_l$ , measured at 400 r.p.m. in  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{O}$ . Also indicated are the corresponding concentrations of  $\text{H}_2\text{O}$  in the binary system  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{O}$  and in the ternary system  $\text{CrO}_{3(\text{sat})}$ - $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{O}$ .  $T = 20^\circ\text{C}$ .

sulphur was observed. Typical profiles illustrating the behaviour are shown in Fig. 11b and 11c. The Auger data suggest that the current oscillations are related to changes in the anodic surface film.

#### 4. Discussion

The present study shows that anodic dissolution of chromium in  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  electro-polishing electrolytes takes place in the transpassive potential region and yields a hexavalent reaction product. According to the literature, bichromate in concentrated sulphuric acid is in equilibrium with sulphatochromate  $\text{CrO}_3\text{SO}_4^{2-}$  [15] and the existence of similar equilibria in phosphoric acid is probable.

In all electrolytes studied, electropolishing was achieved only if dissolution occurred under mass transport control. The 65%  $\text{H}_3\text{PO}_4$ , 20%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  solution yielded mass transport-controlled currents at all temperatures studied, ranging from 6 to  $70^\circ\text{C}$  (Fig. 3). At  $20^\circ\text{C}$ , mass transport-limited currents and electropolishing were observed also in solutions containing 20–85%  $\text{H}_3\text{PO}_4$ , 0–65%  $\text{H}_2\text{SO}_4$ , 15%  $\text{H}_2\text{O}$  or 71–85%  $\text{H}_3\text{PO}_4$  and 15–29%  $\text{H}_2\text{O}$ . On the other hand, in 85%  $\text{H}_2\text{SO}_4$  and 15%  $\text{H}_2\text{O}$  the plateau currents were not limited by mass transport (Fig. 6) and resulting surfaces were not polished.

Different observations lead to the conclusion that the limiting current involves film formation on the anode and that the transport of reaction

products from the surface into the bulk is rate limiting. Firstly, the value of the limiting current is drastically reduced by addition of  $\text{CrO}_3$  to the electrolyte (Fig. 7). According to the proposed model the rate of transport is proportional to the concentration difference between anode surface and bulk, with the surface concentration under steady-state conditions corresponding to the saturation concentration. Adding  $\text{CrO}_3$  to the electrolyte reduces the concentration difference and hence the value of the limiting current. Secondly, the data of Fig. 5 show that increasing the  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  ratio at constant  $\text{H}_2\text{O}$  content decreases the value of the limiting current. This is consistent with the fact that the solubility of  $\text{CrO}_3$  in concentrated sulphuric acid is an order of magnitude smaller than in phosphoric acid. Solubility data for the system  $\text{CrO}_3$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  are given in [16]. They show that in highly concentrated  $\text{H}_2\text{SO}_4$  either one of two solids may precipitate, i.e.  $\text{CrO}_3$  or  $\text{CrO}_3 \cdot \text{SO}_3$ . The equilibrium solubility of the latter species is lower. Solubility values of  $\text{CrO}_3$  in  $\text{H}_3\text{PO}_4$  determined in the present work are given in Fig. 12. The saturation concentration decreases with increasing  $\text{H}_3\text{PO}_4$  concentration. Also shown in Fig. 12 are values of the limiting current measured during anodic dissolution of chromium in  $\text{H}_3\text{PO}_4$ - $\text{H}_2\text{O}$  mixtures. They decrease with increasing acid concentration in a similar manner to the  $\text{CrO}_3$  saturation concentration.

A quantitative comparison of the magnitude of the measured limiting currents with those predicted theoretically for a salt film precipitation



model requires knowledge of such physical properties as solubility, diffusion coefficient and viscosity. For the ternary system  $\text{H}_3\text{PO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ , these are not available. On the other hand, they are known for the system  $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$ , except for the diffusion coefficient. The latter can be estimated from the work of Krichmar *et al.* [17] who measured the diffusion coefficient of copper ions in concentrated phosphoric acid and found it to vary inversely with viscosity. Assuming in a first approximation the diffusion coefficient of hexavalent chromium to be equal to that of  $\text{Cu}^{2+}$ , one calculates from the Levich equation for the limiting current density at  $20^\circ\text{C}$  and 400 r.p.m. in a 85%  $\text{H}_3\text{PO}_4$  and 15%  $\text{H}_2\text{O}$  solution ( $\rho = 1.689\text{ g cm}^{-3}$ ,  $\eta = 78.87 \times 10^{-2}\text{ g cm}^{-1}\text{ s}^{-1}$  [18],  $D = 1.1 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ ,  $C_{\text{sat}} = 1.87\text{ mol dm}^{-3}$ ,  $n = 6$ ) a value of  $i_l = 0.11\text{ A cm}^{-2}$ . Considering the assumptions made, the order of magnitude agreement of this value with the measured value of  $i_l = 0.2\text{ A cm}^{-2}$  is satisfactory.

Further support for the proposed film precipitation model comes from the observation that the time for the establishment of steady-state conditions at the beginning of the limiting current plateau is much larger than can be explained by the theory of non-steady-state mass transport at a rotating disc electrode [19], and varies with potential. Due to the high viscosity of the electrolyte and the possible existence of metastable species [16], nucleation of the surface film is apparently slow and the required supersaturation is potential dependent.

The formation at the anode of  $\text{CrO}_3$  or  $\text{Cr}_2\text{O}_7^{2-}$  involves oxygen ions which are furnished by diffusion of water from the bulk to the anode. The question of whether  $\text{H}_2\text{O}$  could be the diffusion limiting species therefore deserves a brief discussion. In Fig. 12 the  $\text{H}_2\text{O}$  concentrations in  $\text{H}_3\text{PO}_4$  and in ternary solutions saturated with  $\text{CrO}_3$  are indicated. These decrease with increasing acid concentration in a similar manner to the measured limiting current. A semi-quantitative estimation for the experimental conditions used above for  $\text{CrO}_3$  (400 r.p.m.  $20^\circ\text{C}$ , 85%  $\text{H}_3\text{PO}_4$  and 15%  $\text{H}_2\text{O}$ ) with the assumptions  $n = 2$  (three molecules  $\text{H}_2\text{O}$  per hexavalent chromium),  $D = 1.1 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$  (as above), and  $C_{\text{H}_2\text{O}} = 14.07\text{ mol dm}^{-3}$  yields a

theoretical value of  $i_l = 0.29\text{ A cm}^{-2}$ . This is approximately three times higher than that calculated for diffusion of hexavalent chromium, but still of the same order of magnitude as the measured value of  $0.2\text{ A cm}^{-2}$ . Based only on an estimation of the limiting current, an acceptor mechanism involving  $\text{H}_2\text{O}$  diffusion, therefore, cannot be entirely excluded. However, in view of the different observations presented before, a film precipitation mechanism involving rate limiting transport of hexavalent chromium is more probable. In particular, the strong effect of  $\text{CrO}_3$  additions on the value of the limiting current (Fig. 7) cannot be explained otherwise, the  $\text{H}_2\text{O}$  content being affected only a little by the presence of  $\text{CrO}_3$  (Fig. 12).

Under certain conditions in the limiting current region, pronounced current oscillations were observed (Figs 2, 4, 8). These are attributed to interfacial reactions such as film breakdown or adsorption processes. Auger electron spectroscopy performed on electrodes polarized at the limiting current in solution containing sulphuric acid (Fig. 11) indeed showed a different surface composition below and above the region of current oscillations. The presence of sulphur in the latter case indicates that sulphate ions accede to the metallic surface if the potential is sufficiently high, and adsorb there. A similar behaviour has previously been observed during electropolishing of titanium in perchloric acid-containing media where chloride was found on the surface after dissolution at sufficiently high potentials [20]. The behaviour bears some resemblance to pitting, which requires a critical potential for film breakdown and involves interactions between electrolyte anions and the oxide film [21].

Under present conditions current oscillations occur in the potential region where the surface state, characterized by AES, changes. Similar current oscillations have been observed with other electropolishing systems [20, 21] and they are not specifically related to the presence of sulphate. In the present experiments current oscillations were also observed in phosphoric acid solutions. According to Glarum and Marshall [22] current oscillations may occur in the presence of a negative impedance, and the oscillation period is affected by the electrolyte

resistance. The pitting-type mechanism suggested above is believed to be responsible for the negative impedance behaviour under present conditions.

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