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The electrochemical study of a chromium plating bath. II. Chromium metal and surface film formation

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The investigation of the electrode reactions occurring at metal and vitreous carbon cathodes in the standard chromium electroplating solution, 200 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4, has been continued and this paper considers the mechanism of deposition of metallic chromium and the role of surface films in this process. It is confirmed that chromium deposition occurs at potentials negative to − 1.6 V versus Hg/Hg_2SO_4 and under galvanostatic or potentiostatic conditions, the current efficiency is 30–45%. Moreover at a vitreous carbon electrode, potential step experiments lead to rising *I–t* transients characteristic of instantaneous nucleation and three dimensional phase growth.

At potentials just prior to metal deposition the potential sweep and step experiments show clear evidence for the formation of a strongly passivating film (this may be in addition to an existing less passivating layer). The important of the film varies with H_2SO_4 concentration and at intermediate concentrations, potential step experiments lead to unusual oscillating *I–t* transients.

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1. Introduction

It is widely accepted [1–15] that a film on the cathode surface layer plays an important role in the electrodeposition of chromium metal from the bath, 200 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4. The film is considered to contain chromium in an oxidation state between six and zero and there is also radioactive tracer evidence that it also contains sulphate [9, 10, 14]. There has also been a recent suggestion [15] that the cathode is, in fact, covered by two layers, a loose outer structure and a compact inner film. Most of the evidence for the existence of the film and, indeed, the electrochemistry of the bath results from galvanostatic experiments. The literature of recent years, however, would demonstrate that potentiostatic techniques are more likely to lead to a clear picture for the mechanism of a metal deposition process, particularly in a system involving complex chemistry which is certainly the case for chromium plating. Hence the present study employing mainly potential sweep and step methods was commenced.

The preceding paper reported a study using potentiostatic methods which confirmed that the first step in the reduction of chromium(VI) is the formation of Cr(III) and demonstrated that the process is diffusion controlled with respect to sulphate and that at most cathodes the potential for the reaction is determined by the removal of a passivating oxide film from the cathode. This paper considers the formation of chromium metal and the processes involving surface films which precede metal formation.

2. Experimental procedure

In general, the instrumentation, cells, chemicals and experimental procedures were described in the preceding paper [16]. The electrodes used to prepare samples for electron microscopy were discs, diameter 5 mm and thickness about 2 mm, held in position in the cell in PTFE tube. The electron micrographs were recorded using a Cambridge Stereoscan 150.

The current efficiencies for chromium deposition were determined by dissolution of the electroplate in concentrated HCl, additions of HNO_3 and analysis of the resulting solution by atomic

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absorption spectroscopy using an Instrumentation Laboratory Inc. Model 157 spectrometer.

3. Results

Figure 1 shows the *I–E* curves resulting from linear potential sweep experiments at rotating C and Ni electrodes in 200 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4. Visual observation of the electrode shows that Cr metal deposition occurs in the potential region of the final increase in current at very negative potentials. It can be seen that Cr deposition occurs at less negative potentials at Ni (this would also be the case for Cu) than on C. The curves also show the peaks for the Cr(VI) to Cr(III) reduction at − 1.12 V with Ni and at − 0.13 V with C and it was shown in the previous paper that in the region of the peaks, these electrode processes are mass transfer controlled with respect to sulphate ion. For a single mass transport controlled process, however, the *I–E* curve at potentials negative to those for reduction would show a current plateau. This is not the case with any electrode material and it was suggested that this behaviour was due to partial passivation by a mixed oxidation state chromium oxide film. Of more concern in this paper, however, is the much larger dip in current observed at more negative potentials i.e. − 1.35 V at Ni and − 1.50 V at C but prior to the formation of metal. The curve at C also shows an increase in current in the range − 1.0 V to − 1.4 V. The current dip is even more marked at a stationary C electrode, see Fig. 2. Indeed the current in the region 1.47 V to − 1.58 V drops to zero. The large nucleation loop at the negative end of the potential scan should also be noted; the cathodic current in the potential region − 1.5 V to − 1.7 V is much larger on the reverse scan than on the sweep towards negative potentials.

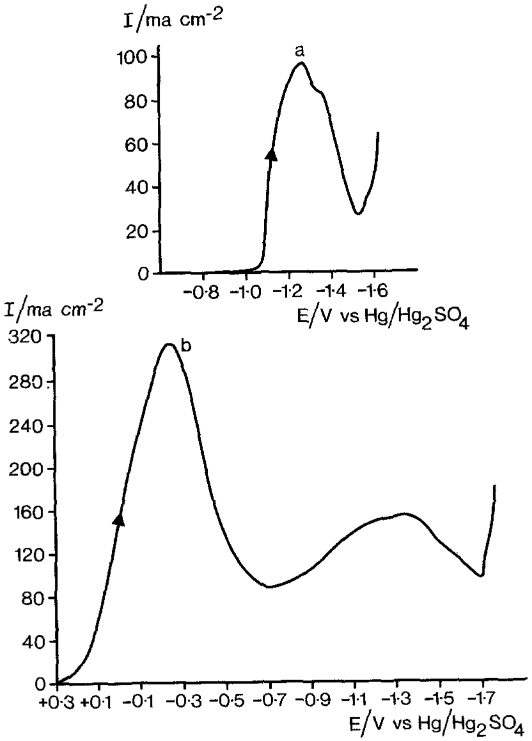

Fig. 1. *I–E* curves at rotating disc electrodes in a solution of 200 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4. (a) Ni, (b) vitreous C. Rotation rate 10 Hz. Potential scan rate 0.01 V s^{-1}.

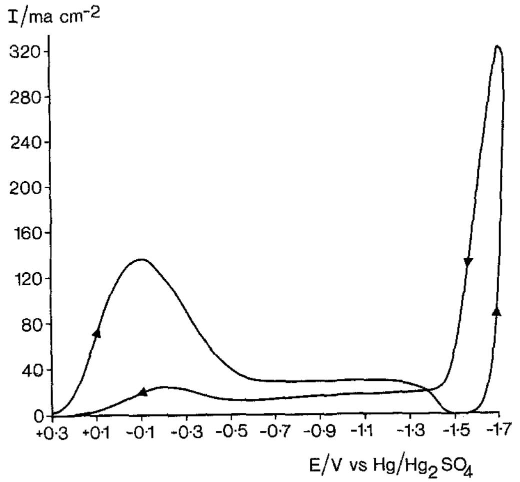

Fig. 2. Cyclic voltammogram at a vitreous C electrode in 200 g dm^{-3} CrO_3 + 2 g dm^{-3} H_2SO_4. Potential scan rate 0.03 V s^{-1}.

A series of experiments were carried out to check the current efficiency for Cr metal deposition under both potentiostatic and galvanostatic conditions. The cathode was a rotating Cu electrode and in each experiment the plating process was continued until a charge of 90 C cm^{-2} had been passed. The surface was then washed thoroughly with distilled water before the Cr was dissolved in concentrated HCl and the resulting solution was analysed for Cr^{3+} by atomic absorption spectroscopy. The results are reported in Table 1. It can be seen that over a wide range of conditions the current efficiency lies in the range 20–45%, noticeably higher than that obtained in

Table 1. Current efficiencies for the deposition of Cr on a rotating Cu electrode (1200 rpm) from 200 g dm^{-3} CrO_3 + H_2SO_4 as a function of plating conditions. Plating charge 90 C cm^{-2}. Temperature 20° C.

Galvanostatic deposition (2 g dm^{-3} H_2SO_4)		*Potentiostatic deposition* (2 g dm^{-3} H_2SO_4)			*Variation of [H_2SO_4]* (E = − 1.70 V versus Hg/Hg_2SO_4)		
I (mA cm^{-2})	*Current efficiency* (%)	− E (V versus Hg/Hg_2SO_4)	*Measured I* (mA cm^{-2})	*Current efficiency* (%)	*[H_2SO]* (g dm^{-3})	*Measured I* (mA cm^{-2})	*Current efficiency* (%)
180	31.5	1.6	84– 72	22.8	1	210–180	33.9
350	36.8	1.7	190–150	36.5	2	190–150	36.5
540	42.2	1.8	330–240	41.3	4	195–140	40.0
		2.0	570–480	43.3	6	195–140	34.8
					10	195–135	31.5
					15	165–125	26.3

industrial practice but similar to those reported by Gerischer and Käppel [5]. It is also apparent that the conclusions from the potentiostatic and galvanostatic depositions are the same, i.e., the current efficiency improves as the electrode potential is made more negative, and that deposition is possible at − 1.7 V at 1–15 g dm^{-3} H_2SO_4 concentrations. Galvanostatic deposition at 80 mA cm^{-2} was, however, not possible at the higher H_2SO_4 concentrations.

The deposition of Cr on vitreous C could also be studied using potential step techniques. Figure 3 shows the I–t transients resulting from a series of potential steps. At short times, there is always a falling I–t response associated presumably with the reduction of Cr(VI) to Cr(III) and with film formation, but on the timescale shown in the figure, rising I–t transients are observed. Complete analysis of the transients is not possible because each transient clearly shows at least three different components. Figure 4, however, shows $I^{1/2}$ versus t plots for the lower current density regions of the transients. It can be seen that good linear plots are obtained consistent with a mechansim of deposition involving instantaneous nucleation and three dimensional growth. Such an interpretation is con-

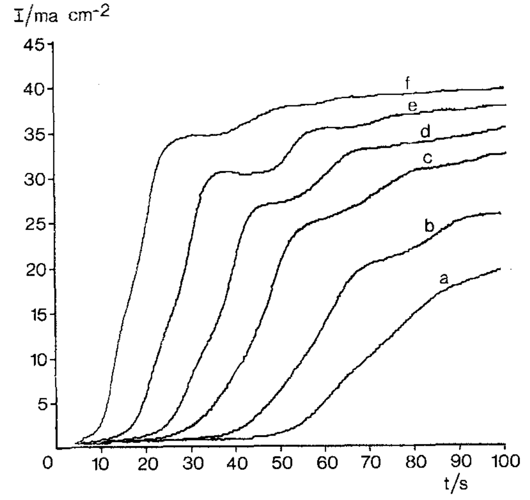

Fig. 3. I–t transients recorded at a vitreous C electrode in 200 g dm^{-3} CrO_3 + 2 g dm^{-3} H_2SO_4 in response to potential steps from + 0.30 V to (a) − 1.50 V, (b) − 1.52 V, (c) − 1.54 V, (d) − 1.56 V, (e) − 1.58 V, (f) − 1.60 V.

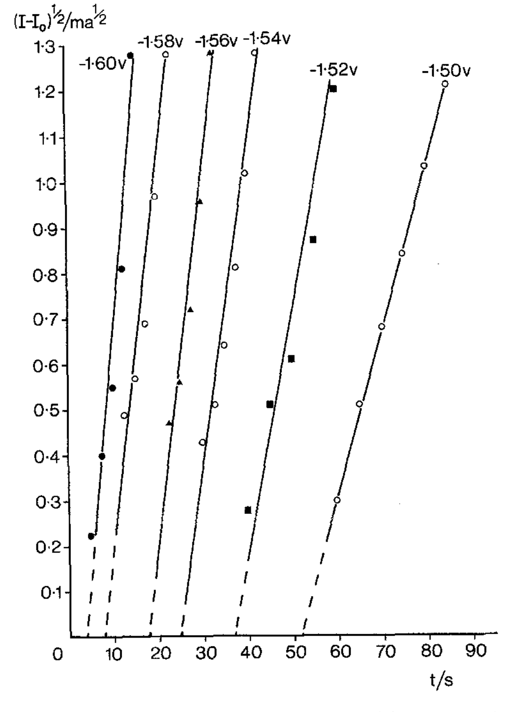

Fig. 4. Data of Fig. 3 replotted as $(I - I_0)^{1/2}$ versus t. I_0 is the low current density just before the start of the rising transient.

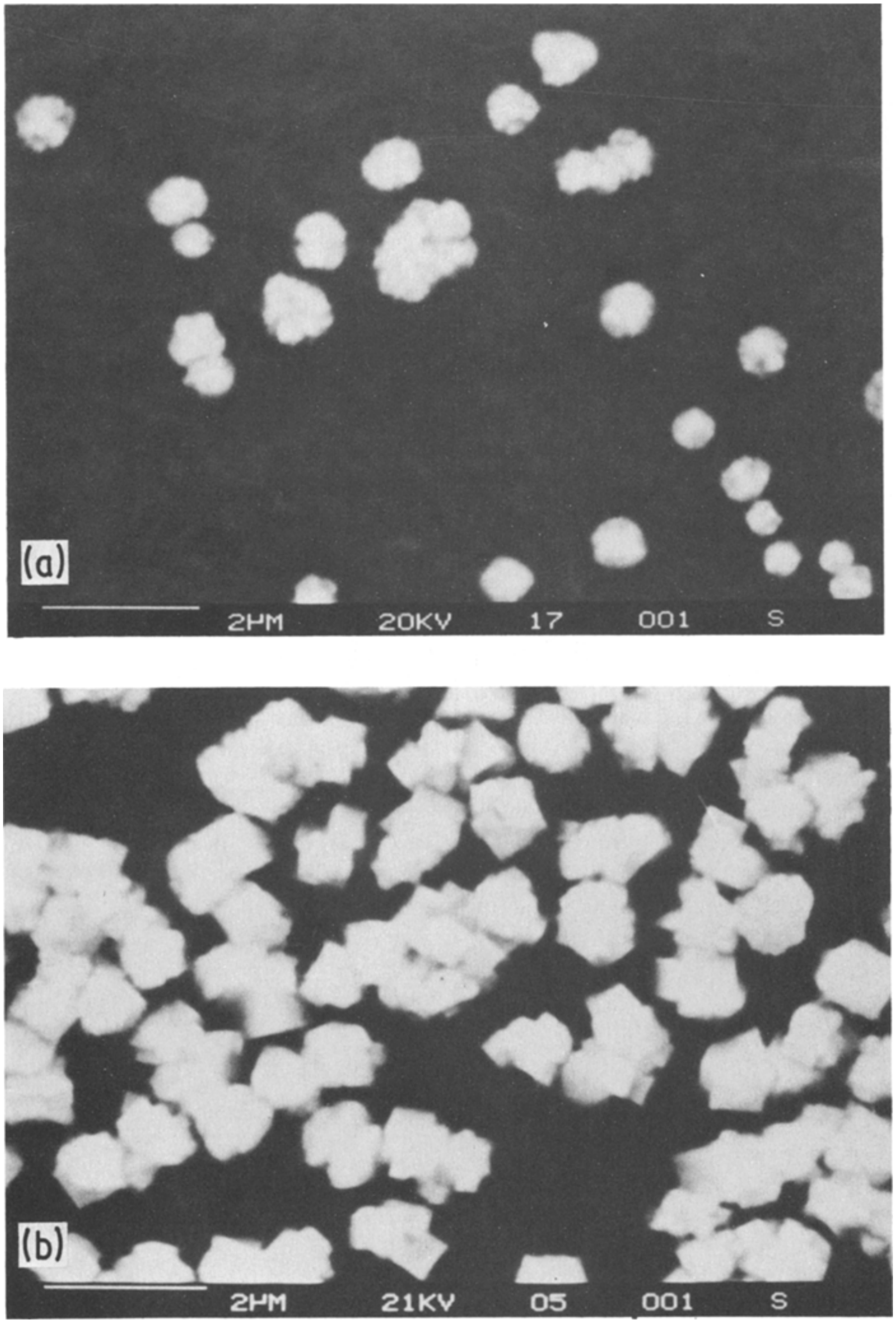

Fig. 5. Electron micrographs of chromium centres grown on a vitreous C electrode at — 1.56 V versus Hg/Hg_2SO_4. Plating bath as previous figures. Growth time (a) 30 s, (b) 100 s.

firmed by electron microscopy, Fig. 5; the chromium centres can clearly be seen to have similar sizes and the growth is three dimensional. On the other hand the $I^{1/2}$–t plots do not have the expected behaviour. Over the potential range of the figure, — 1.50 to — 1.60 V, the slopes of the $I^{1/2}$–t plots are almost independent of potential and the major change is a decrease in the intercept on the time axis with increasing potential. Such behaviour is most likely to be explained by a deposition process whose rate is determined by a chemical reaction preceding the electron transfer process leading to Cr(O) (c.f. molybdenum [17]) and a nucleation process which required an induction time. Such an induction time could arise from processes within a film and it should also be noted that the background of Fig. 5(a) is quite unlike an electron micrograph of a vitreous carbon surface which had not been exposed to electrochemistry in the chromium plating bath. Rising *I–t* transients were not observed with either Ni or Cu electrodes. Potential step experiments in the bath 200 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4 always led to falling transients while cyclic voltammograms did not show nucleation loops associated with Cr deposition. This may indicate that the kinetics of nucleation are much faster at the metal electrodes and any nucleation phenomenon is hidden by the charge for the other concurrent processes [Cr(VI) to Cr(III) reduction, film formation and hydrogen evolution].

During the experiments, an interesting observation was made concerning the potential region of the dip in current just positive to Cr deposition; in some conditions potential step experiments to potentials in this region led to strong and regular oscillations of the current with time, see Fig. 6. Such *I–t* responses could be observed with Ni, Cu or C electrodes but only for a restricted range of solution compositions, the important factor being the ratio of $[CrO_3]/[H_2SO_4]$ which had to lie in the range 100/2 to 100/6 with the optimum being 100/4. The behaviour for a Ni electrode in the solution 50 g dm^{-3} CrO_3 and 2 g dm^{-3} H_2SO_4 is illustrated in Fig. 6. Oscillating currents could be recorded between − 1.43 V and − 1.54 V; over a potential range between − 1.43 V and − 1.48 V; potential has little effect on the frequency or amplitude of the oscillations but Table 2 shows the effect of the CrO_3 concentration. In the potential range − 1.43 V to − 1.46 V, the oscillations continue almost indefinitely but at more negative potentials the oscillations eventually die out and beyond − 1.50 V this occurs after only a few oscillations. When the oscillations die out, the current smooths out at the lowest current density.

Table 2. Characteristics of the current oscillations at a Ni electrode as a function of CrO_3 concentration. $[CrO_3]/[H_2SO_4] = 200/8$

$[CrO_3]$ (g dm^{-3})	*Oscillation*		*Average* I (mA cm^{-2})
	Amplitude (mA cm^{-2})	*Frequency* (Hz)	
50	175	2	115
100	310	4	225
150	445	5	275
200	500	7	350

The current oscillations must arise because of competition of two processes at the surface, one involving electron transfer and leading to the formation of a strongly passivating film and the other leading to the breakdown of the film and reactivation of the electrode surface. This latter process may be pitting caused by proton or chemical dissolution of the film by H_2SO_4. The role of H_2SO_4 is indicated because the oscillations only appear at intermediate H_2SO_4 concentrations, at low concentrations the surface remains strongly passivated while at high concentrations the surface does not passivate. The role of electron transfer in the film formation process is suggested by the narrow range of potentials where oscillations are observed. The nature of the electrode reaction leading to the strongly passivating film beyond − 1.35 V is uncertain. The less passivating film immediately negative to the peak may well be the mixed oxide resulting from interaction of Cr(III) species with a Cr(VI) anion but the second film must be the result of a further reduction process. At Ni or Cu electrodes this could be the hydrogen evolution reaction leading to hydroxide ion but although *I–E* curves in some conditions at C show a wave at an appropriate potential, it does not appear to lead to hydrogen gas and may therefore be due to the Cr(III)/Cr(II) couple. The formation of a film dependent on hydroxide ion is perhaps more likely.

4. Discussion

It was concluded in the previous paper that at Cu, Ni, Cr and C, the chromium(VI) first undergoes reduction to chromium(III) and at the metals, the potential for this process is determined by the removal of an oxidised film from the metal. The limiting current for the Cr(VI)/Cr(III) process is determined by the mass transport of sulphate to the electrode surface and immediately beyond the potential of the peak, the *I–E* curves show evidence for passivation and it was suggested that this is due to a surface layer of a mixed oxidation state chromium oxide formed by reaction of a chromium(III) and chromium(VI) species. The chromium(VI) to chromium(III) reduction continues to occur, albeit at a reduced rate probably because the film dissolves continuously in H_2SO_4 as it reaches the surface. It was also noted that at

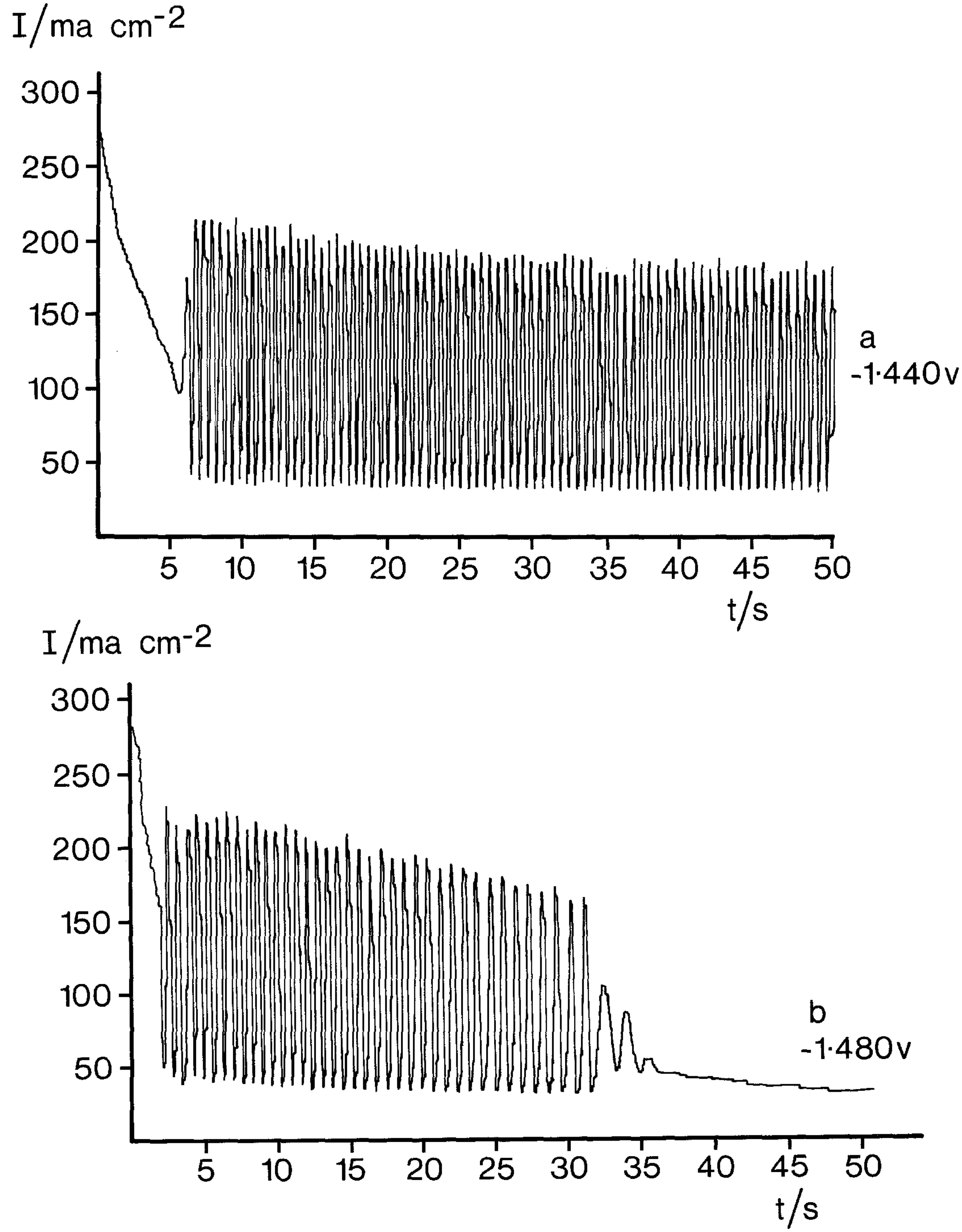

Fig. 6. *I–t* responses to a potential step from – 0.60 V to (a) – 1.44 V, (b) – 1.48 V, (c) – 1.52 V. Rotating Ni electrode in 50 g dm^{-3} CrO_3 + 2 g dm^{-3} H_2SO_4.

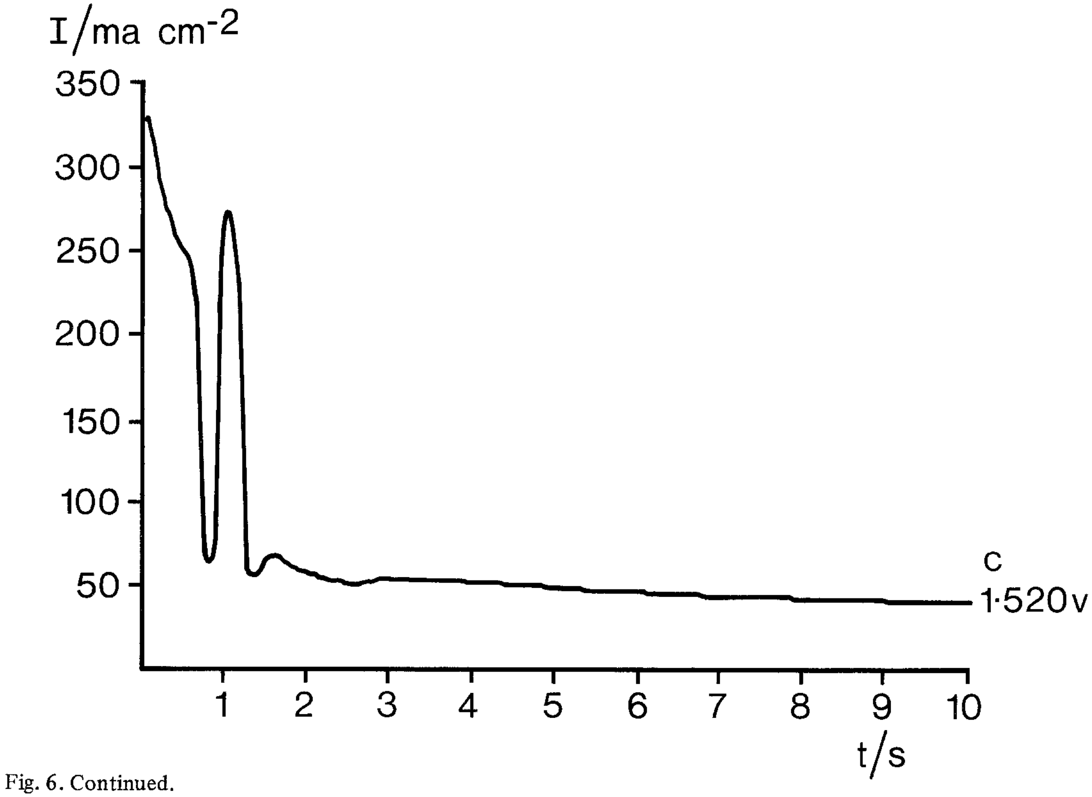

Fig. 6. Continued.

Cu and Ni, a mass transport limited reduction of proton to hydrogen gas could be observed. In this paper it has been shown that in solutions containing less than 4 g dm^{-3}, a more strongly passivating film is formed at potentials negative to this process and the current for the Cr(VI)/Cr(III) process may drop to 10% of the mass transport limited current (and indeed to zero at C). Chromium metal deposits at even more negative potentials [9].

At the beginning of a galvanostatic or a potentiostatic plating process, the reduction of Cr(VI) to Cr(III) will be the first reaction to occur. The electrode will then form a passivating film before Cr metal deposition commences. It seems to be the general concensus of opinion that the metal is formed by diffusion of chromium ions through the layer. This seems to us unlikely because, firstly, such a mechanism requires the continuous conversion of a chromium oxide/sulphate lattice into a Cr metal lattice with quite different composition, dimensions and structure, and secondly, the current density at which deposition occurs implies an unreasonably high rate of diffusion of ions through the film. An alternative role for the passivating film is to create the conditions essential for nucleation of the metal phase. In galvanostatic conditions, the film is essential to force the potential to a negative value where nucleation can occur. Moreover, there is little compelling evidence for a surface film during growth of the Cr layer once nucleation has occurred and it is therefore possible to envisage a growth phase where reduction of Cr(VI) and H$^+$ are parallel reactions. The reduction of Cr(VI) will proceed via Cr(III), and maybe Cr(II), and a role of sulphate ion is to prevent the precipitation of intermediate oxidation states. The observation that chromic sulphate does not reduce to the metal is readily understood in view of the known chemistry of Cr(III), its complexes are only substituted very slowly and it is likely that the Cr(III) intermediate in the electrode reaction is different from that formed by dissolution of chromic sulphate i.e., the mechanism is [5, 18, 19]

$$\begin{tikzcd}
\mathrm{Cr(VI)} \arrow[r, "+3e"] & {[\mathrm{Cr(III)}]_A} \arrow[r, "+3e"] \arrow[d, shift left] & \mathrm{Cr} \\
\mathrm{Cr_2(SO_4)_3} \arrow[r] & {[\mathrm{Cr(III)}]_B} \arrow[u, shift left] &
\end{tikzcd}$$

The amount of Cr(III) in solution depends on the relative rate of reduction and substitution of $[Cr(III)]_A$ and the above mechanism also explains the difference between fresh and aged Cr(III) species.

The observations in this paper are also in accord with earlier proposals that two surface layers are formed prior to metal formation [15]. Oscillating phenomena have also been noted during galvanostatic experiments [8, 12] although it is not clear that the potential range was the same as in this paper. The oscillating current in the potential range of the strongly passivating film is further evidence for the need to limit the sulphate ion in solution; the film is only stable enough to allow nucleation of the metal at low sulphate ion concentration.

5. Conclusions

At room temperature using both galvanostatic and potentiostatic conditions in the laboratory, the current efficiency for chromium deposition is higher than that obtained in industrial practice.

There are two surface films involved in the electrochemistry of the chromium plating bath.

It is suggested that the importance of the strongly passivating surface film is to create the conditions essential for nucleation of the metallic phase. Once formed the metal layer grows by reduction of Cr(VI) to Cr(O) via Cr(III).

The role of the sulphate ion is to allow the formation of a soluble Cr(III) species but its concentration must be limited if the strongly passivating film necessary for nucleation of the metallic phase is to be formed.

At intermediate H_2SO_4 concentrations, an unusual *I–t* response is observed at potentials just prior to metal formation.

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