

STUDIES OF CHROMIUM PLATING FROM LOW CONCENTRATION ELECTROLYTES

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Chromium plating is generally carried out from electrolytes containing chromic acid along with a small quantity of sulphate in the absence or presence of fluorine compound. Normally fairly concentrated solutions with 250 to 400 g/l chromic acid are used. Such a high concentration of chromic acid leads to excess drag-out losses, and higher effluent treatment costs. These considerations have necessitated investigations abroad on the usefulness of low concentration solutions. In this paper the authors highlight the results of studies on low concentration electrolytes. Experiments were carried out with varying concentrations of chromic acid from 50 g/l to 250 g/l in the presence of 1% sulphate by means of Hull cell tests in order to determine the basic solution composition. Current efficiency and rate of build-up were also determined in the case of selected compositions. The effect of boric acid or lanthanum oxide were investigations in certain solution compositions.

Keywords: Plating, chromic acid and boric acid or lanthanum oxide

INTRODUCTION

The rapid worldwide growth in chromium plating since its commercialisation in 1924, is due to a combination of outstanding properties of electrodeposited chromium like high resistance to atmospheric corrossions at ordinary and elevated temperature, high hardness with wear resistance and low coefficient of friction [1,2]. Chromium plating may be divided into two general categories namely decorative and hard. Hard chromium plating which is of functional importance forms the subject of this paper.

Generally chromium plating is being carried out from 250 g/l chromic acid electrolytes containing 2.5 g/l sulphuric acid as a minor constituent apart from a small concentration of trivalent chromium specifically provided in the bath by means of addition of oxalic acid or citric acid. Elsewhere low concentration electrolytes [3,4] had been experimented with limited success. Investigations carried out with low concentration electrolytes are reported in this paper.

EXPERIMENTAL

Hull cell studies

Preliminary experiments were carried out using solutions containing chromic acid and sulphuric acid at different concentration levels, the former ranging from 50 to 250 g/l and the latter ranging from 0.125 to 2.5 g/l at 323 K. Finally, the effects of temperature were studied with the chosen low concentration bath for the temperatures 303, 313, 323 and 333 K. The cathode used was 100 x 60 x 0.25 mm mild steel plate in each case and lead-tin alloy anode of 62.5 x 62.5 x 2.0 mm size was used. A cell current of 10 A was employed for 5 minutes in each case.

Current efficiency and rate of build up studies

The electrodeposition assembly consisting of two lead-tin alloy anodes and one steel cathode of equal size, (30 x 30 x 2 mm) was dipped in 2 litre solution taken in a wide glass vessel. One anode was positioned on either side of the cathode. A regulated direct current supply unit (IMEC,

Ahmedabad) with very low ripple was used along with a coulombmeter in the circuit. The solution was agitated occasionally by using a heater cum magnetic stirrer. The temperature of the experimental solutions was maintained ± 273 K of the desired value. The specimen was weighed before and after deposition and cathode current efficiency and deposit thickness in each case calculated.

Throwing power studies

The throwing power was determined with Haring Blum cell making use of the Field formula. The cell consisted of a rectangular P.V.C. container of internal size 150 x 50 x 50 mm with sheet metal cathodes of 90 x 50 x 1 mm size filling the entire cross section at both ends and the perforated lead-tin alloy anode of the same size. The latter was placed between the cathodes so that its distance from one of the cathodes was one fifth of its distance from the other. The mass of metal deposited on each of nearer cathode (C_n) and the farther cathode (C_f) was found by weighing before and after each experiment and the ratios $C(C_n/C_f)$ calculated.

$$\text{Throwing power (\%)} = \frac{K - C}{K + C - 2} \times 100$$

where K is the distance ratio between the anode to the farther cathode and anode to the nearer cathode.

Micro-hardness measurements

The values of micro hardness of electrodeposited chromium obtained from different chromium plating electrolytes at different conditions of current density and temperature were determined on the Vickers scale by using a Russian made PMT - 3 Microscope - Hardness meter. The diamond pyramid was pressed into each of the deposit under a load of 50 g for 15 seconds and the indentation diagonal measured after removal of the load. The deposit microhardness was determined with the formula

$$\text{Hardness} \left(\frac{\text{kg}}{\text{mm}^2} \right) = \frac{1854 \times P}{d^2}$$

where P is the load applied in grams and 'd' the indentation diagonal in micrometers.

Porosity measurements

The porosity of an electrodeposit being generally a measure of its corrosion resistance, that of each chromium deposit was evaluated by means of Ferroxy test.

RESULT AND DISCUSSION

Hull cell studies

The results are presented in the Figs. 2 to 6. Fig. 2 pertains to the effect of varying concentrations of CrO_3 and H_2SO_4 in solutions at 323 K and with 10A cell current. From Figs. 2 to 6, it may be seen that a low concentration of chromic acid (50 g/l) can give rise to bright chromium over the high and middle current density areas. If the chromic acid concentration is increased to 150 g/l a bright plating range is obtained. With a further increase in chromic acid concentration the bright region gradually changes into a semibright one while the area corresponding to the absence of deposition is confined only to the low current density area in all the case studied. From the above observations the following composition was considered as the optimum for further studies.

Chromic acid	50 g/l and 150 g/l
Sulphuric acid	0.5 g/l and 2.0 g/l
Temperature	323 K

Current efficiency studies

Tables I to III present the results of current efficiency studies with different electrolytes under different conditions.










	No deposit
	Semi bright
	Slight brown
	Brown film
	Brown dots
	Bright
	Yellow film
	Slate coloured film
	Satin

Fig. 1: Code for hull cell patterns

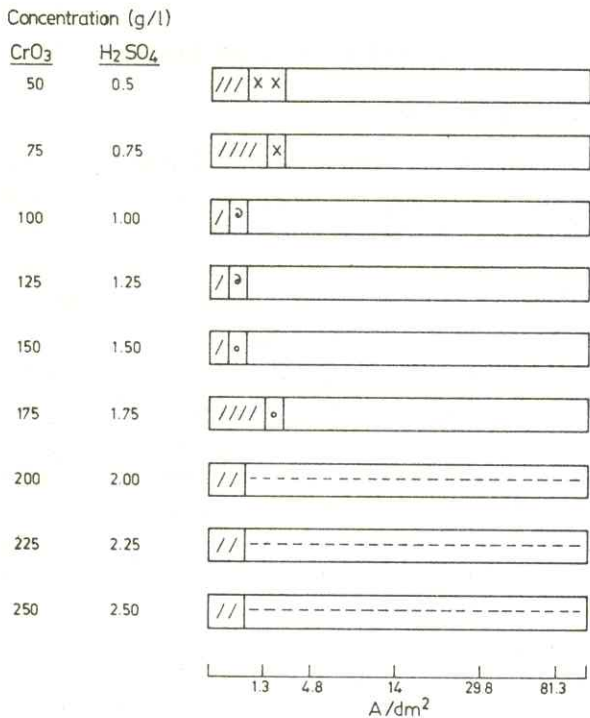


Fig. 2: Appearance of hull cell patterns from $\text{CrO}_3 - \text{H}_2\text{SO}_4$ electrolytes at 323K

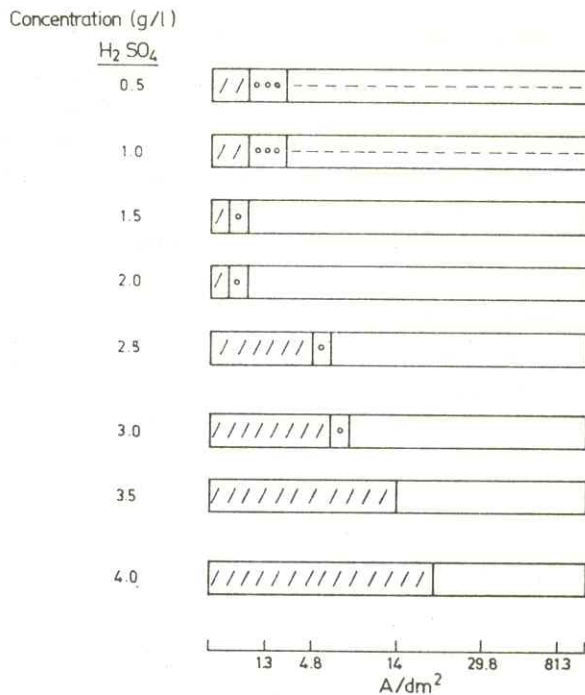


Fig. 4: Appearance of hull cell patterns from 150 g/l CrO_3 containing different quantities of H_2SO_4 at 323 K

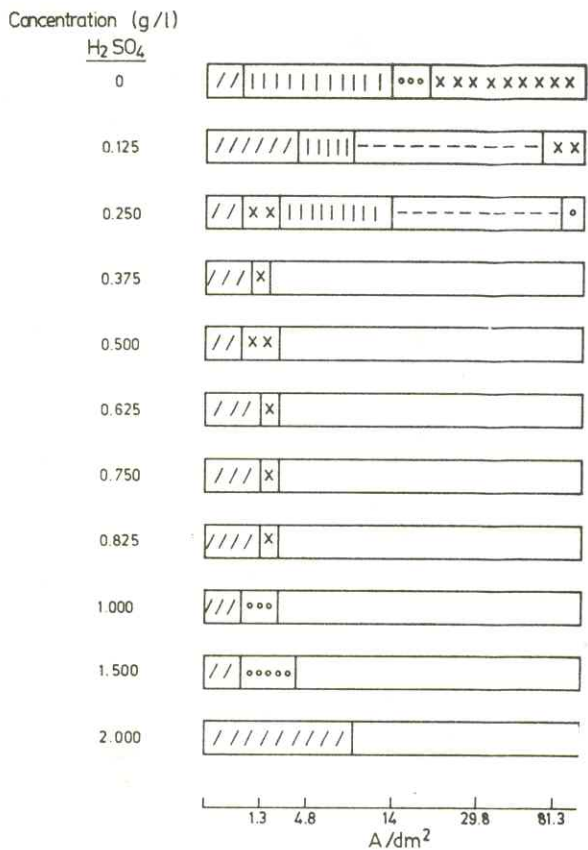


Fig. 3: Appearance of hull cell patterns from CrO_3 electrolytes (50 g/l CrO_3) H_2SO_4 at various concentrations at 323 K

The current efficiency increases with an increase of current density. In certain cases there is a marginal but not significant increase in current efficiency with increasing concentration of bath constituents. Additions of boric acid or lanthanum oxide do not cause any significant change in current efficiency.

The rate of build-up always increases with current in proportion to current efficiency.

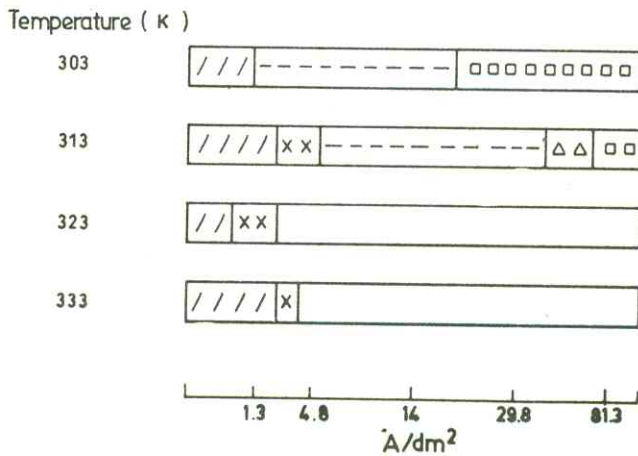


Fig. 5: Appearance of hull cell patterns from 50 g/l CrO_3 electrolytes with 0.5 g/l H_2SO_4 at various temperatures

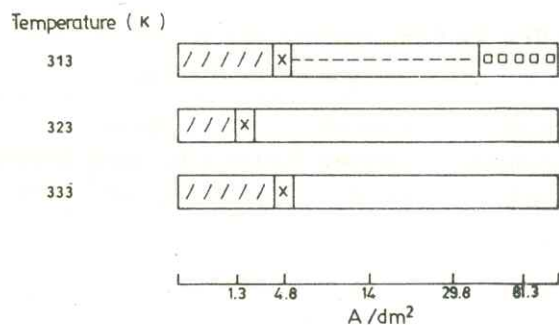


Fig. 6: Appearance of hull cell patterns from 50 g/l CrO_3 containing 0.75 g/l H_2SO_4 and at various temperatures

Deposit appearance

From Tables IV to VI it is seen that bright deposits can be obtained from either of the baths at 323 K for all the current densities (7-42 A/dm^2) in the presence or absence of additives other than H_2SO_4 .

Deposit microhardness measurements

Tables IV to VI show that the hardness values do not significantly change when the concentrations of different constituents are changed. The values show a slight increase generally with La_2O_3 addition.

TABLE I: Cathode current efficiency and rate of build up at different concentrations of chromic acid and sulphuric acid

Bath ingredients (g/l)		Current density (A/dm^2)	Cathode current efficiency (%)	Rate of build up ($\mu\text{m}/\text{h}$)
CrO_3	H_2SO_4			
50	0.50	7	9.3	3.3
50	0.50	21	15.0	14.5
50	0.50	35	17.0	28.3
50	0.50	42	17.7	34.0
50	0.75	7	9.5	3.4
50	0.75	21	16.8	16.2
50	0.75	35	17.6	22.3
50	0.75	42	19.6	37.7
150	1.00	7	9.3	3.3
150	1.00	21	15.6	14.2
150	1.00	35	17.2	27.8
150	1.00	42	19.0	30.7
150	1.50	7	9.3	3.3
150	1.50	21	14.8	14.2
150	1.50	35	17.4	28.1
150	1.50	42	19.9	38.3
150	2.00	7	8.9	3.2
150	2.00	21	15.0	14.4
150	2.00	35	16.7	27.0
150	2.00	42	20.4	39.3

TABLE II: Cathode current efficiency and rate of build up at different concentrations of chromic acid, sulphuric acid and boric acid

Bath ingredients (g/l)			Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{h}$)
CrO_3	H_2SO_4	H_3BO_3			
150	2.00	5	7	8.5	3.00
150	2.00	5	21	13.4	12.90
150	2.00	5	35	16.9	27.40
150	2.00	5	42	16.8	32.40
150	2.00	10	7	7.7	2.70
150	2.00	10	21	13.3	25.60
150	2.00	10	35	15.5	25.20
150	2.00	10	42	19.0	36.50
150	2.00	20	7	7.5	2.70
150	2.00	20	21	13.9	13.30
150	2.00	20	35	16.8	27.30
150	2.00	20	42	16.9	32.50
50	0.75	20	7	8.4	2.97
50	0.75	20	21	13.9	13.33
50	0.75	20	35	16.8	27.30
50	0.75	20	42	16.9	32.50

Assessment of deposit porosity

Deposit porosity is substantially lower and completely absent in many cases with the addition of lanthanum oxide for any of the baths for the current density range of 28-42 A/dm^2 deposits from solutions with or without H_3BO_3 generally have a high degree of porosity.

TABLE III: Effect of lanthanum oxide on deposition characteristics at 323 K

Bath ingredients (g/l)			Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{h}$)
CrO_3	H_2SO_4	La_2O_3			
50	0.75	1.00	7	9.70	3.5
50	0.75	1.00	21	15.50	14.9
50	0.75	1.00	35	17.90	28.9
50	0.75	1.00	42	18.80	36.1
50	0.75	2.00	7	8.80	3.2
50	0.75	2.00	21	15.80	15.2
50	0.75	2.00	35	18.60	30.1
50	0.75	2.00	42	19.20	37.0
150	2.00	3.00	7	7.55	2.7
150	2.00	3.00	21	13.20	12.7
150	2.00	3.00	35	16.30	26.4
150	2.00	3.00	42	17.30	33.3

TABLE IV: Characteristics of deposits from CrO₃ — H₂SO₄ solutions at 323 K

Bath ingredients (g/l)		Current density (A/dm ²)	Nature of deposit	Micro hardness (kg/mm ²)	Porosity (%)
CrO ₃	H ₂ SO ₄				
50	0.50	7	**	—	60
50	0.50	28	Bright	715	10
50	0.50	42	"	715	40
50	0.75	7	"	—	80
50	0.75	28	"	799	40
50	0.75	42	"	799	40
150	1.00	7	"	—	80
150	1.00	28	"	678	30
150	1.00	42	"	715	10
150	1.50	7	"	—	50
150	1.50	28	"	715	20
150	1.50	42	"	799	20
150	2.00	7	"	—	50
150	2.00	28	"	847	40
150	2.00	42	"	715	40

** Bright with yellow film at middle

TABLE V: Characteristics of deposits from electrolytes with H₃BO₃ addition

Bath ingredients (g/l)			Current density (A/dm ²)	Nature of deposit	Micro hardness (kg/mm ²)	Porosity (%)
CrO ₃	H ₂ SO ₄	H ₃ BO ₃				
150	2.00	5	7	UB	—	40
150	2.00	5	28	"	755	50
150	2.00	5	42	"	755	40
150	2.00	10	7	"	—	60
150	2.00	10	28	"	847	20
150	2.00	10	42	"	847	40
150	2.00	20	7	"	—	70
150	2.00	20	28	"	756	0
150	2.00	20	42	"	715	0
150	0.75	10	7	"	—	100
50	0.75	10	28	"	756	10
50	0.75	10	42	"	715	30

UB = Uniform bright

TABLE VI: Characteristics of deposit from La₂O₃ containing solutions at 323 K

Bath ingredients (g/l)			Current density (A/dm ²)	Nature of deposit	Micro hardness (kg/mm ²)	Porosity (%)
CrO ₃	H ₂ SO ₄	La ₂ O ₃				
50	0.75	1	7	Bright	—	5
50	0.75	1	28	"	799	0
50	0.75	1	42	"	715	—
50	0.75	2	7	"	—	5
50	0.75	2	28	"	799	0
50	0.75	2	42	"	799	30
50	0.75	3	7	"	—	0
50	0.75	3	28	"	847	0
50	0.75	3	42	"	847	0
150	2.00	3	7	"	—	0
150	2.00	3	28	"	715	0
150	2.00	3	42	"	715	0

CONCLUSION

The investigations reported indicate that chromium electrodeposits can be obtained from more dilute solutions than usually employed and that addition of La₂O₃ significantly minimises their porosity.

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