

EFFECT OF VARIOUS SULPHATES ON CHROMIUM PLATING

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For chromium plating, along with chromic acid a small quantity of sulphate ion is very much essential. In the absence of sulphate ion the chrome bath will not produce any bright deposit but will produce only brown film. The sulphate ion is normally introduced as sulphuric acid at a ratio of 100:1 to chromic acid. In this paper, in order to study the effect of other sulphate ions, it is aimed to study the effect of cations associated with sulphates. The sulphate to the chrome bath was introduced in the form of sulphuric acid, sodium sulphate, ammonium sulphate, potassium sulphate and chromium sulphate. Hull Cell experiments were carried out to study the nature of the deposit. Plating experiments were also carried out to study the current efficiency, rate of buildup, porosity, hardness, and nature of deposit and the results are presented.

Keywords: Chromium plating, sulphates, Hull Cell experiments

INTRODUCTION

Chromium plating, an industrially important coating, is at present mostly produced from conventional chrome bath consisting of chromic acid and sulphuric acid at a concentration ratio of 100:1. It is well known that for chromium plating along with chromic acid a small quantity of sulphate ion is very much essential. In the absence of sulphate ion the chrome bath will not produce any bright chromium deposit but will produce only brown film. Thus sulphate ion is one of the important constituent in chromium plating and few workers have carried out studies on the effect of sulphate concentration of chromium plating and the effect of chromic acid to sulphate ratio on chromium plating.

A microscopic study of the formation of cathodic films on steel during electrolysis of chromium plating solutions at various chromic acid to sulphate ratios have been reported [1]. The characteristic properties of electrodeposited chromium from solutions with varying sulphate chromic acid concentrations have been studied [2]. Influence of sulphates and silicofluorides on the properties of the cathodic film formed during electrodeposition of chromium was studied [3]. Role of sulphate ion in the chrome plating electrolyte

and the effect of sulphate on decorative nickel-chromium electrodeposition were also studied and reported [4,5].

In order to study the effect of various cations associated with sulphate, the sulphate to the chromic acid was introduced as sulphamic acid, sodium sulphate, potassium sulphate, ammonium sulphate and chromium sulphate and Hull Cell and plating experiments were carried out to study the nature of the deposit, current efficiency, rate of build up, porosity and microhardness. The results are presented in this paper.

EXPERIMENTAL

For the chromium plating experiments mild steel specimens were used. The surface was prepared by mechanical, chemical as well as electrochemical methods as given in Table I. Technical grade chromic acid along with other laboratory chemicals were used for this study. A three phase rectifier with A.C. ripple less than 5% and calibrated ammeters were used. The temperature of the electrolyte was maintained at 323 ± 1 K with the help of electrical glass immersion heaters.

Hull Cell experiments

Hull Cell experiments were carried out in order to observe the nature of the deposit over a range of current densities.

TABLE I: Results on cathode efficiency and rate of build up at different current densities from chromium plating bath containing chromic acid 250 g/l, oxalic acid 4 g/l and sulphuric acid at different concentrations at 323 K for 1 hour duration

Concn of SO_4^{2-} (H_2SO_4) (g/l)	Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{hr}$)	Porosity (%)	Hardness (Kg/mm^2)	Nature of deposit
1.25	15.5	14.93	10.39	20	980	A
	31.0	11.96	16.66	10	970	B
2.50	15.5	9.40	6.54	25	980	A
	31.0	16.28	22.66	10	980	A
5.00	15.5	9.30	6.47	30	950	A
	31.0	13.46	18.75	25	960	C

A = Bright Cr deposit; B = Bright Cr with pores

C = Semi bright Cr deposit

Polished and cleaned mild steel cathodes of 100 x 60 x 0.25 mm size were used with a cell current of 7 A and for a duration of 5 minutes. A 267 ml Hull Cell of standard dimensions and 93:7 lead tin alloy anode was used for this study.

Current efficiency experiments

Mechanically polished and cleaned mild steel specimens of 30 x 30 mm size were used as cathodes in an electrodeposition assembly consisting of two 93:7 lead tin alloy anodes on either side of the cathode. The plating bath was agitated occasionally during use to maintain the temperature ± 1 K. The cathodes were weighed before and

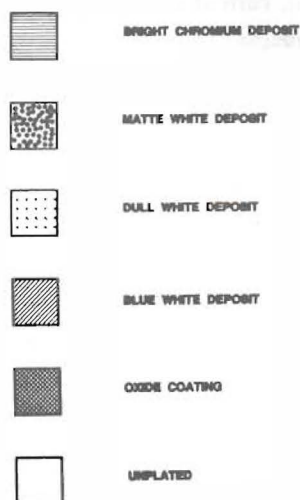


Fig. 1: Codes used for the various nature of the deposits

CONCENTRATION OF H_2SO_4 g/l

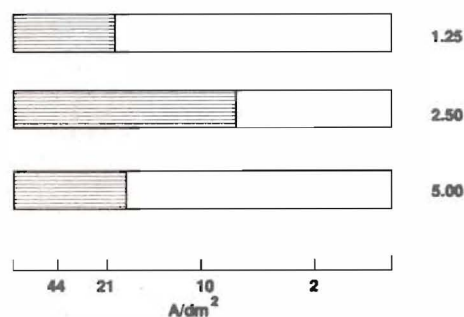


Fig. 2: Effect of varying concentration of SO_4^{2-} (H_2SO_4) in conventional chrome bath

after the experiment. The current efficiency and the rate of buildup was found out gravimetrically in each case.

The values of microhardness of electrodeposited chromium obtained from different chromium plating electrolytes at different conditions of current density and temperature were determined by using Russian made PMT-3 microscope at a load of 50 g. The Vickers microhardness of the deposit in kg/mm^2 was determined by using the appropriate formula.

The porosity of chromium electrodeposits obtain under different conditions was evaluated by means of ferroxyl test.

RESULTS AND DISCUSSION

The results of the various studies carried out are presented in Figs. 1-6 and Tables I-V.

Hull Cell studies

Figs. 1-6 present the Hull Cell patterns obtained under different conditions. Fig. 1 indicates the different codes employed to describe the nature of the chromium deposits obtained under various conditions. Fig. 2 presents the Hull

CONCENTRATION OF Na_2SO_4 g/l

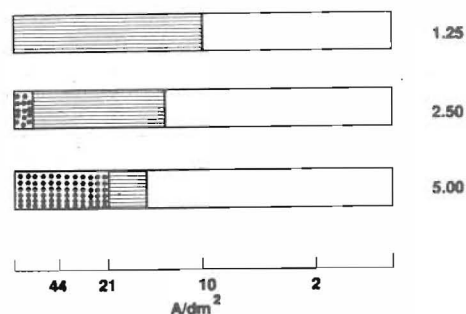


Fig. 3: Effect of varying concentration of SO_4^{2-} (Na_2SO_4) in conventional chrome bath

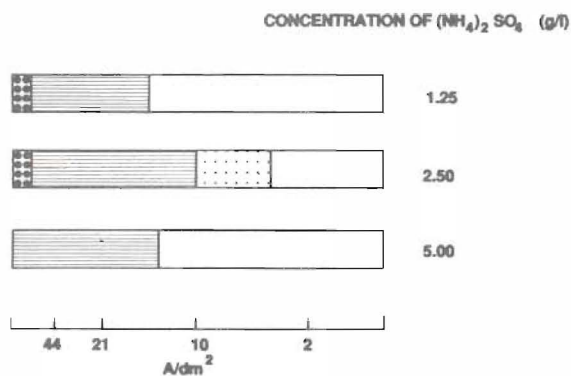


Fig. 4: Effect of varying concentration of $SO_4^{2-}(NH_4)_2SO_4$ in conventional chrome bath

Cell patterns obtained with varying concentrations of sulphuric acid added to the 250 g/l chromic acid and when operated at 323 K with a cell current of 7 A for 5 minutes duration. From the figure it may be seen that when the sulphuric acid concentration is 1.25 g/l in 250 g/l chromic acid concentration bright chromium deposit is obtained only at the high current density area but when sulphuric acid concentration is increased to 2.5 g/l the bright deposit region extends to a wider level. Further increase in concentration of sulphuric acid once again the bright region decreases thereby indicating that 2.5 g/l sulphuric acid concentration along with 250 g/l chromic acid is ideal to produce bright chromium deposit over a wide current density range.

Fig. 3 presents the effect of addition of sodium sulphate instead of the conventionally added sulphuric acid to the 250 g/l chromic acid when operated at 323 K and at 7 A. cell current for 5 minutes duration. From the figure it may be seen that 1.25 g/l sodium sulphate along with 250 g/l chromic acid produces bright chromium deposits over a wide current density range. Further increase in concentration of

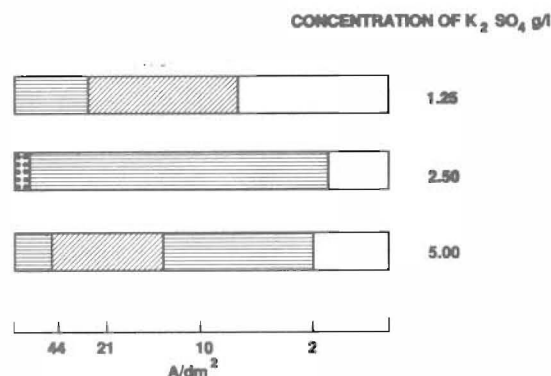


Fig. 5: Effect of varying concentration of $SO_4^{2-}(K_2SO_4)$ in conventional chrome bath

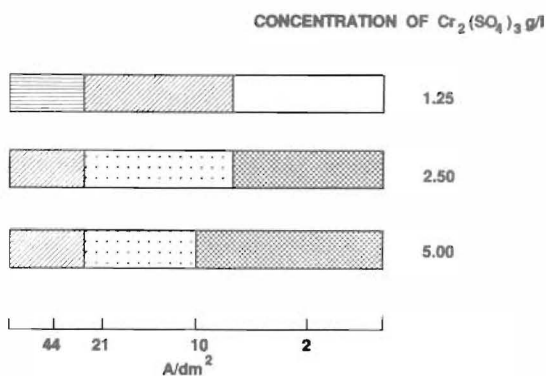


Fig. 6: Effect of varying concentration of $SO_4^{2-}(Cr_2(SO_4)_3)$ in conventional chrome bath

sodium sulphate does not produce any improvement in the nature of the deposit. This indicates that even a small concentration of sodium sulphate namely 1.25 g/l is sufficient to produce bright chrome deposit.

Fig. 4 indicates the effect of addition of varying concentration of ammonium sulphate to the 250 g/l chromic acid when operated at 323 K and at 7 A cell current for 5 minutes duration. This figure indicates that when the concentration of ammonium sulphate is 2.5 g/l, the bath produces bright chromium over a wide current density range. This indicates that 2.5 g/l ammonium sulphate along with 250 g/l chromic acid is more suitable to produce quality deposits at 323 K.

TABLE II: Results on current efficiency and rate of build up at different current densities from chromium plating bath containing chromic acid 250 g/l, oxalic acid 4 g/l and sodium sulphate at different concentrations at 323 K for 1 hour duration

Concn of SO_4^{2-} (Na_2SO_4) (g/l)	Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu m/hr$)	Porosity (%)	Hardness (Kg/mm^2)	Nature of deposit
1.25	15.5	5.19	3.61	50	940	A
	31.0	4.03	5.61	50	920	B
2.50	15.5	9.89	6.88	40	950	C
	31.0	15.40	21.44	30	950	D
5.00	15.5	9.03	6.28	50	900	E
	31.0	19.02	26.47	10	890	F

A = Bright rough Cr deposit

B = Matte white rough pits Cr deposit

C = Bright Cr deposit; D = Milky white Cr deposit

E = Matte white Cr deposit

TABLE III: Results on current efficiency and rate of build up at different current densities from chromium plating bath containing chromic acid 250 g/l, oxalic acid 4 g/l and ammonium sulphate at different concentrations at 323 K for 1 hour duration

Concn of SO_4^{2-} ($(\text{NH}_4)_2\text{SO}_4$) (g/l)	Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{hr}$)	Porosity (%)	Hardness (Kg/mm^2)	Nature of deposit
1.25	15.5	12.52	8.71	30	950	A
	31.0	12.82	17.84	30	960	B
2.50	15.5	11.78	8.20	40	970	A
	31.0	16.62	23.14	20	980	C
5.00	15.5	6.37	4.43	50	920	C
	31.0	13.17	18.34	40	900	C

A = Semibright Cr deposit

B = Semi bright Cr with pits at the edge

C = Bright Cr deposit

Fig. 5 presents the effect of addition of different concentrations of potassium sulphate in 250 g/l chromic acid, when operated at 323 K and 7 A cell current for a duration of 5 minutes. From the figure it may be seen that when the concentration of potassium sulphate is increased to 2.5 g/l bright chromium deposit is obtained more or less on the entire area of the Hull Cell plate. Thus it can be seen that the addition of 2.5 g/l potassium sulphate to 250 g/l chromic acid is more beneficial to produce bright deposit over a wide range of current density.

Fig. 6 presents the Hull Cell patterns obtained for different concentrations of chromium sulphate in 250 g/l chromic acid and when operated at 323 K with a cell current of 7 A for 5 minutes duration. From the study it may be concluded that the chromium sulphate addition at all concentrations studied does not produce bright deposit but produces mostly dull white deposit.

From these studies it is confirmed that along with chromic acid the presence of a sulphate anion is necessary to produce bright chromium deposit. It may also be pointed out from these studies that the cations associated with sulphate anion also plays an important role in modifying the deposit. Thus from the Hull Cell patterns obtained it may be concluded that the potassium cation associated with sulphate anion is highly beneficial in producing bright chrome deposit over a wide current density range.

Current efficiency studies

The results of the current efficiency experiments carried out are given in Tables I-V.

Table I presents the results when varying concentrations of sulphuric acid is added to 250 g/l chromic acid and operated at 323 K and at 15.5 A/dm^2 and 31 A/dm^2 . It may be seen from the table that the cathode efficiency increases with increase in current density. But on the other hand the cathode efficiency decreases with increase in concentration of sulphuric acid. It may be concluded from the table that 2.5 g/l sulphuric acid is more suitable to be added to 250 g/l chromic acid electrolyte to obtain maximum current efficiency.

Table II presents the results on the current efficiency experiments carried out when varying concentrations of sodium sulphate added to 250 g/l chromic acid and operated at 323 K and at 15.5 A/dm^2 and 31.0 A/dm^2 . From the results it may be seen that chromium plating electrolyte containing 250 g/l chromic acid and 5 g/l sodium sulphate exhibits high cathode efficiency than the other conditions studied.

From Table III it can be noted that 2.5 g/l ammonium sulphate may be added to 250 g/l chromic acid in order to obtain high current efficiency under normal working conditions.

From Table IV, which indicates the effect of potassium sulphate in chrome bath operated at 323 K and at 15.5 A/dm^2 and 31 A/dm^2 , it can be seen that the current efficiency increases marginally with increase in concentration of potassium sulphate. From Table V it can be

TABLE IV: Results on cathode efficiency and rate of build up at different current densities from chromium plating bath containing chromic acid 250 g/l, oxalic acid 4 g/l and potassium sulphate at different concentrations at 323 K for 1 hour duration

Concn of SO_4^{2-} (H_2SO_4) (g/l)	Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{hr}$)	Porosity (%)	Hardness (Kg/mm^2)	Nature of deposit
1.25	15.5	11.22	7.81	25	950	A
	31.0	13.36	18.60	20	960	B
2.50	15.5	9.99	6.95	30	990	A
	31.0	15.32	21.33	20	980	A
5.00	15.5	9.27	6.54	50	940	A
	31.0	16.45	23.03	20	960	A

TABLE V: Results on cathode efficiency and rate of build up at different current densities from chromium plating bath containing chromic acid 250 g/l and chromium sulphate at different concentrations at 323 K for 1 hour duration

Concn of SO_4^{2-} ($\text{Cr}_2(\text{SO}_4)_3$) (g/l)	Current density (A/dm^2)	Current efficiency (%)	Rate of build up ($\mu\text{m}/\text{hr}$)	Porosity (%)	Hardness (Kg/mm^2)	Nature of deposit
1.25	15.5	12.55	8.70	20	920	A
	31.0	17.35	24.15	10	900	B
2.50	15.5	6.61	4.60	30	940	B
	31.0	13.14	18.29	30	930	B
5.00	15.5	1.57	1.09	50	920	C
	31.0	8.01	11.15	40	900	B

A = Bright Cr deposit; B = Semi bright Cr deposit

C = Light grey Cr deposit

seen that the current efficiency falls down with increase in concentration of chromium sulphate.

Nature of the deposit

The results of the studies on the nature of the deposit obtained after plating are produced in Tables I-V. From these results it may be seen that the addition of either H_2SO_4 or K_2SO_4 at 1% concentration to chromic acid is more favourable to produce bright acceptable deposits.

Rate of buildup

The results of the experiments carried out on the rate of build up of chrome deposits under different conditions studied are given in Tables I-V. From the tables it may generally be seen that the rate of build up of chrome deposits increases with increase in current density.

Microhardness of deposits

The results of measurements of the microhardness values for deposits obtained from different electrolytes under different conditions are given in Tables I-V. From the results it may be seen that 2.5 g/l sulphuric acid addition to 250 g/l

chromic acid produces more hard deposits. In a similar manner the addition of potassium sulphate to the 250 g/l chromic acid also produces more hard deposits under all operating conditions studied when compared to other sulphates containing chrome baths.

Porosity

From the results as given in Tables I-V it may be seen that in general the porosity of chrome deposits decreases with increase in thickness. From the experiments carried out it may be seen that the deposits produced under different operating conditions from electrolytes containing 250 g/l chromic acid along with 2.5 g/l of H_2SO_4 or K_2SO_4 exhibits less porous chromium deposits.

CONCLUSION

From the limited experiments carried out it may be concluded that the sulphate anion is necessarily to be added to the chromic acid to produce chrome deposit and the ratio of chromic acid to sulphate may be preferably 100:1. The following chromium plating bath composition is recommended to produce bright chrome deposit with high current efficiency, high microhardness and with less pore density.

Chromic acid: 250 g/l; Potassium sulphate: 2.5 g/l; Temperature: 323 K; Current density: 15.5-31.0 A/dm^2

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