

EFFECT OF TRIVALENT IRON AND TRIVALENT CHROMIUM IONS ON CHROMIUM PLATING

RM KRISHNAN, S SRIVEERARAGHAVAN, SOBHA JAYAKRISHNAN
C JOSEPH KENNADY*, R SEKAR AND NIRMALA BABY**

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

* Geep Industrial Syndicate Limited, Allahabad 211 001. INDIA

** Holy Cross College, Tiruchirapalli 620 002. INDIA

Chromium electrodeposition is nowadays considered as one of the most important electrodeposition processes. Chrome deposits are used both for decorative and for functional applications. A thin, blue-tinged chrome deposit is normally applied on nickel undercoats in the decorative nickel-chromium finish. Such nickel-chromium decorative finishes are applied on a number of decorative articles like cycle components, automobile components, household articles, office furnitures etc. In industry a thick chromium deposit is used as hard chromium and is used to coat on a number of components which are resistant to wear and tear. The high hardness of chromium resists wear and tear and improves the service life of the components. Such an industrially important chromium is normally deposited from conventional chrome bath consisting of 250 g/l chromic acid and 2.5 g/l sulphuric acid and operated at 323 K and at a current density of 15.5 and 46.5 A/dm². Chromium is deposited from hexavalent chromium using insoluble anodes. However, during the normal working of the bath, there is a gradual increase in Cr³⁺ concentration in the bath due to the incomplete oxidation of Cr³⁺ and Cr⁶⁺ at the anode. Buildup of Iron(III) in chrome bath occurs in a number of ways. They are a) carry over from previous operations due to poor washing of the components b) dissolution of substrate when jobs are allowed to be in chrome bath without current, c) due to anodic etching from the plating bath itself and d) etching of fallen articles remaining in the bath. Thus the entry of Cr³⁺ and Fe³⁺ are inevitable in the chrome bath. In order to study the effect of iron and trivalent chromium in the production of chrome deposit the study was undertaken and the results on the nature of the deposit, current efficiency, rate of build up, hardness and porosity are presented in this paper.

Keywords: Chromium plating, trivalent iron, electrodeposition, trivalent chromium

INTRODUCTION

Chromium is an important metal very familiar to electroplaters and it is used for a variety of applications starting from the thin decorative layer over bright nickel to the thick layers which are hard, abrasion and wear resistant [1,2]. Chromium plating is mostly carried out from the conventional type of bath consisting of chromic acid and sulphuric acid. A major problem encountered in chromium plating is the bath contamination that builds up with time [2,3].

The deposition of metallic chromium on the cathode is accompanied by the evolution of hydrogen and the partial

reduction of Cr⁶⁺ to Cr³⁺. The main function of lead-tin alloy anode is to oxidise back the Cr³⁺ to Cr⁶⁺ [4,5]. If these reactions do not occur proportionately at the two electrodes, Cr³⁺ concentration will go high in the bath.

Contamination of chromium bath with iron impurity is almost inevitable. The main reasons [4] for this are allowing the job to remain in the bath without current, etching that may occur at low c.d. areas, reverse etching if carried out from the plating bath itself and non-removal of fallen steel articles from the bath.

The effects of iron and trivalent chromium in conventional chrome bath are investigated and results are reported in this paper.

EXPERIMENTAL

Conventional chromium bath of composition chromic acid 250 g/l and sulphuric acid 2.5 g/l was prepared. All plating studies were carried out on cold rolled steel specimens using Pb-Sn (7% Sn) alloy as anode after the normal preplating treatments of degreasing, electrocleaning and acid dipping.

Hull Cell studies were carried out in a 257 ml Standard Hull Cell at a cell current of 7 A for a duration of 5 mts. For determining the nature of deposits, cathode current efficiency and rate of build up, plating was done on 2.5 x 7.5 cm panels at two different current densities of 15.5 and 31.0 A/dm².

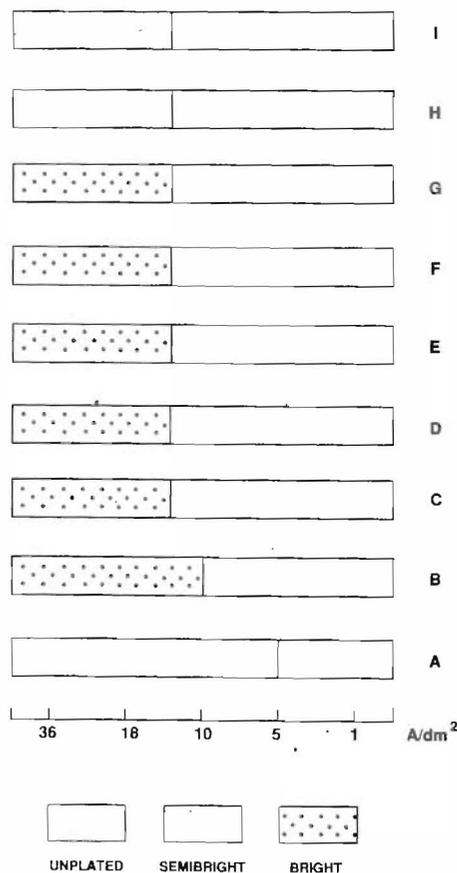


Fig. 1: Effect of varying Cr^{3+} concentration in bath containing chromic acid 250 g/l, sulphuric acid 2.5 g/l, temperature 323 K
Cell current 7 A, Cr^{3+} concentration
A - 1.0, B - 2.5, C - 5.0, D - 7.5, E - 10.0
F - 12.5, G - 15.0, H - 17.5, I - 20 g/l

Panels (2.5 x 7.5 cm) plated with chromium under the various conditions were subjected to microhardness test (in PMT 3 Microscope hardness meter with a load of 50 g) and porosity test (by Ferroxy test).

RESULTS & DISCUSSION

Hull Cell studies

Results of Hull Cell studies are shown in Figs. 1 and 2. When trivalent chromium (Cr^{3+}) concentration was 1.0 g/l, chromium deposit obtained was semibright in appearance (Fig. 1). At 2.5 g/l Cr^{3+} concentration bright chromium was obtained at c.d. above 10 A/dm². This shows that a small amount of trivalent chromium is essential to get attractive bright chromium plating. With further increase in Cr^{3+} concentration upto 15 g/l bright chromium deposit could be obtained. At Cr^{3+} concentrations of 17.5 g/l and above chromium deposit becomes semi bright. Thus it is observed that Cr^{3+} concentration of about 2.5-15 g/l (1-6% of chromic

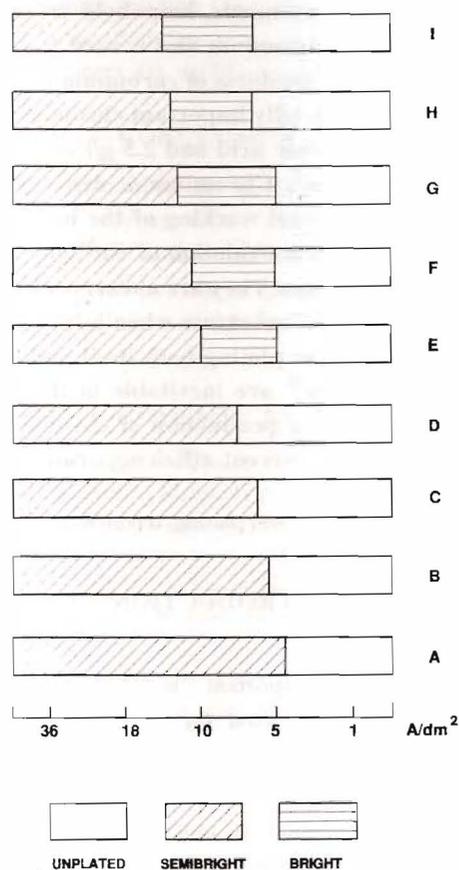


Fig. 2: Effect of varying Fe^{3+} concentration in bath containing chromic acid 250 g/l, sulphuric acid 2.5 g/l, temperature 323 K
Cell current 7 A, Fe^{3+} concentration
A - 1.0, B - 2.5, C - 5.0, D - 7.5, E - 10.0
F - 12.5, G - 15.0, H - 17.5, I - 20 g/l

TABLE I: Influence of Cr³⁺ concentration on electroplating of chromium from bath containing CrO₃ 250 g/l and sulphuric acid 2.5 g/l, temperature 323 K, C.D. 15.5 A/dm²

Concn of Cr ³⁺ (g/l)	Nature of deposit	Current efficiency (%)	Rate of build up (µm/h)	Porosity (%)	Micro hardness (Kg/mm ²)
1.0	SB	11.0	7.7	30	990
2.5	SB	10.8	7.6	30	980
5.0	SB	10.5	7.4	30	970
7.5	SB	10.0	7.0	40	950
10.0	SB	9.2	6.5	50	950
12.5	SB	8.0	5.6	75	930
15.0	SB	6.9	4.8	75	910
17.5	MW	6.2	4.4	80	880
20.0	MW	5.0	3.5	85	870

SB - Semi bright; MW - Matte white

acid concentration) is highly beneficial in producing bright deposit. At concentrations higher than 15 g/l brightness of the chromium deposit gets reduced.

Fig. 2 shows the nature of chromium deposit obtained in presence of varying concentrations of ferric iron in conventional chrome bath. With increase in concentration of iron, the current density region to obtain semibright deposits is shifted to higher c.d. An increase in iron concentration to 10 g/l and higher results in the appearance of brown films at the low c.d. regions.

TABLE II: Influence of Cr³⁺ concentration on electroplating of chromium from bath containing CrO₃ 250 g/l and sulphuric acid 2.5 g/l, temperature 323 K, C.D. 31 A/dm²

Concn of Cr ³⁺ (g/l)	Nature of deposit	Current efficiency (%)	Rate of build up (µm/h)	Porosity (%)	Micro hardness (Kg/mm ²)
1.0	SB	14.3	20.1	10	980
2.5	SB	13.9	19.5	10	980
5.0	SB	13.7	19.2	20	980
7.5	SB	13.6	19.1	25	960
10.0	SB	13.0	18.3	25	940
12.5	SB	12.5	17.6	25	930
15.0	SB	12.1	17.0	30	910
17.5	MW	10.8	15.2	40	890
20.0	MW	9.0	12.6	55	870

Nature of deposit, current efficiency and rate of deposition

Nature of deposit, current efficiency and rate of deposit from conventional chromium bath gets affected when trivalent chromium is introduced in the bath (Tables I and II). Deposit has a semibright appearance upto a Cr³⁺ concentration of 15 g/l, above which the deposit becomes matte white. Current efficiency and rate of build up decrease with increase in Cr³⁺ concentration. This decrease is more pronounced at concentrations higher than 15 g/l both at 15.5 and 31 A/dm² (Fig. 3). Efficiencies are generally higher at 31 A/dm² compared to 15.5 A/dm².

With introduction of ferric iron (Fe³⁺) in the bath the semibright nature of deposit is gradually lost and a brownish tint appears at concentrations higher than 15.0 g/l at 15.5 A/dm² (Table III). However, the appearance remains unaffected even at 20 g/l at an operating c.d. of 31 A/dm². (Table IV). Gradual decrease in efficiency and rate of deposition with increase in iron concentration is observed (Tables III, IV and Fig. 4). The lowering of current efficiency is more clear at 15.5 A/dm². Thus efficiency as well as appearance suffer from iron contamination more at lower current densities.

Porosity and microhardness of deposits

The results of porosity measurements show that more porous deposits are obtained from baths containing Cr³⁺ or Fe³⁺. Porosity is higher with increase in Cr³⁺/Fe³⁺ concentration

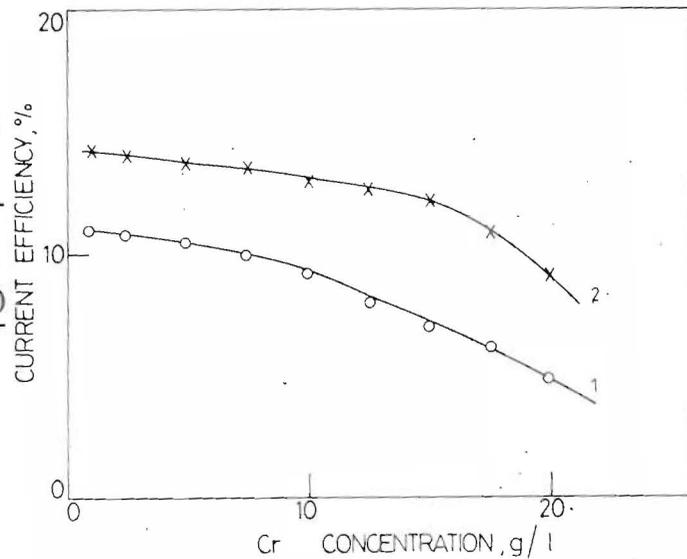


Fig. 3: Variation of current efficiency with Cr³⁺ concentration chromic acid 250 g/l, sulphuric acid 2.5 g/l, temperature 323 K, C.D. 1) 15.5 2) 31.0 A/dm²

TABLE III: Influence of Fe³⁺ concentration on electroplating of chromium from bath containing CrO₃ 250 g/l and sulphuric acid 2.5 g/l, temperature 323 K, C.D. 15.5 A/dm², duration 60 mts

Concn of Fe ³⁺ (g/l)	Nature of deposit	Current efficiency (%)	Rate of build up (µm/h)	Poro-sity (%)	Micro hardness (Kg/mm ²)
1.0	SB	15.6	11.0	10	990
2.5	SB	14.8	10.4	10	980
5.0	SB	13.7	9.6	20	970
7.5	SB	12.4	8.7	20	970
10.0	SB	11.4	8.0	25	920
12.5	SB	10.4	7.3	30	900
15.0	SB	9.6	6.7	30	890
17.5	MW	8.9	6.3	40	860
20.0	MW	7.9	5.6	40	850

SB - Semi bright; MW - Matte white

(Tables I - IV). This shows that the contamination of chrome bath with Cr³⁺ or Fe³⁺ results in increasing the porosity of deposits, which in turn will decrease the corrosion resistance offered by chromium plating.

The microhardness of chromium deposit is found to decrease when plating is carried out from baths containing either Cr³⁺ or Fe³⁺ (Tables I - IV). This observation shows the necessity of avoiding Cr³⁺ and Fe³⁺ contamination in chromium baths as the primary objective of hard chromium plating is the production of a hard, wear and abrasion resistant surface.

TABLE IV: Influence of Fe³⁺ concentration on electroplating of chromium from bath containing CrO₃ 250 g/l and sulphuric acid 2.5 g/l, temperature 323 K, C.D. 31 A/dm²; Nature of deposit = Semibright

Concn of Fe ³⁺ (g/l)	Current efficiency (%)	Rate of build up (µm/h)	Poro-sity (%)	Micro hardness (Kg/mm ²)
1.0	17.5	24.6	5	980
2.5	17.2	24.2	5	970
5.0	16.4	23.1	5	950
7.5	15.8	22.2	5	920
10.0	15.4	21.6	5	890
12.5	14.4	20.2	10	870
15.0	14.0	19.7	10	850
17.5	13.2	18.6	20	820
20.0	12.4	17.4	30	820

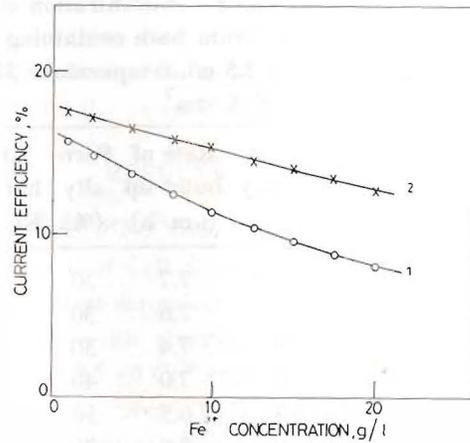


Fig. 4: Variation of current efficiency with Fe³⁺ concentration - chromic acid 250 g/l, sulphuric acid 2.5 g/l, temperature 323 K, C.D. 1) 15.5 — 2) 31.0 A/dm²

CONCLUSION

In a conventional chromium plating bath a small amount of trivalent chromium (2.5 g/l) is beneficial in improving the brightness of chromium deposit. However, higher concentrations of Cr³⁺ above 15 g/l should be avoided as this leads to decrease in brightness, current efficiency and rate of build up and affects the deposit porosity and hardness adversely.

Iron (Fe³⁺) contamination is a serious problem in conventional chrome bath as this produces deposits of unacceptable nature at low current densities, decreases the current efficiency and rate of build up, increases deposit porosity and decreases microhardness of deposits.

From the above results we can conclude that for the best performance of a conventional chromium bath it is necessary to control the concentration of trivalent chromium and eliminate the introduction of trivalent iron in the bath.

REFERENCES

1. J H Lindsay, *Plating Surf Finish*, 84 (1997) 50
2. K Stevens, *Trans Inst Metal Finish*, 75 (1997) 33
3. P Pajunen, *Metal Finishing*, 73 (1995) 50
4. I R Weiner and A Walmsley, *Chromium Plating*, Finishing Publications Ltd., Teddington, U K (1971)
5. RM Krishnan, S Sriveeraraghavan, Sobha Jayakrishnan and S R Natarajan, *Metal Finishing*, 73 (1995) 46