

## Effect of Various Operating Parameters on Trivalent Chromium Electroplating

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### Authors' contributions

*This work was carried out in collaboration between all authors. Author MEH designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript.*

*Authors MAH, MMI, MSI and CMM helped to author MEH by providing valuable suggestions, managing the analysis of this study and also by their respective supervision. All authors read and approved the final manuscript.*

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### ABSTRACT

The investigation was aimed to electrodeposit chromium on mild steel surface from non-toxic trivalent chromium bath instead of toxic hexavalent chromium employed for this purpose. We observed the effect of pH, temperature, current density (C.E.) and also time on to the current efficiency. On the other hand we also observed the effect of the concentration of CrCl<sub>3</sub> on the plating thickness and optical reflectivity. The optimum pH value and bath temperature are 3 and 40°C respectively to obtain highest current efficiency. On the other hand, 90 min deposition time was the best for high current efficiency. We also achieved good current efficiency at 20 A/dcm<sup>2</sup>

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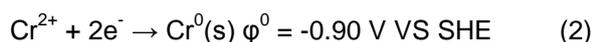
current density. But the plating thickness was increased with increasing the  $\text{CrCl}_3$  concentration in the electrolyte. In case of optical reflectivity, the result is totally opposite. Our findings will contribute to develop the products of plating industries.

*Keywords: Trivalent chromium; current efficiency; plating thickness; optical reflectivity.*

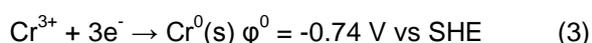
## 1. INTRODUCTION

The chromium electroplating is used commercially due to having some tremendous and uniform properties such as low friction coefficient, exceptional wear resistance and most important one is higher corrosion resistivity [1,2]. As the electrodeposition of trivalent Cr is difficult, so hexavalent Cr is extensively used in plating industries although it has toxic and carcinogenic nature. But the hexavalent Cr bath offers bright surface finish, less porous deposition, good throwing power [3,4]. Considering the toxicity and carcinogenicity, it is better to replace the hexavalent Cr electroplating with the trivalent Cr electroplating due to its low toxic nature and twice larger electrochemical equivalent [5,6].

The mechanism [6] for trivalent Cr electroplating involves two following steps of reaction:

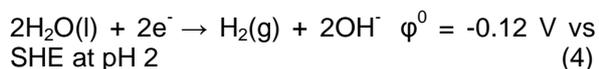


Where  $\phi^0$  denotes standard reduction potential (SRP) at 298K.



Reaction (3) is obtained from accumulation of the above two reactions.

In Cr (III) aqueous bath excessive  $\text{H}_2$  gas evolved at the surface of the cathode: [6]



However, trivalent chromium plating is difficult and cumbersome. There are many complicated factors that restricts the electroplating of Cr as metal from trivalent Cr bath. They are discussed below: [7]

- i) In aqueous solution, the  $\text{Cr}^{3+}$  ions create  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  complex ion that restricts the electrodeposition process of  $\text{Cr}^{3+}$  ions due to decrease the amount of  $\text{Cr}^{3+}$  ions in the bath [7].
- ii) According to the reaction (4), the reduction of  $\text{Cr}^{3+}$  ion to metal Cr is very difficult due

to the reduction potential of  $\text{Cr}^{3+}$  ion is more negative than that of the reduction potential of  $\text{H}_2$ . So it also restricts the electrodeposition process [7].

- iii) Due to the excessive hydrogen evolution reaction on the cathode surface a significant increase of pH value occurred. When the pH exceeds 4.5, then a high molecular weight polymer is formed by a series of reactions on the cathode surface. This process is known as olation. The  $\text{Cr}^{3+}$  ions are trapped inside the complex bridge structure of high molecular weight polymer which restricts the  $\text{Cr}^{3+}$  ion to come out for reduction reaction [7].

In order to solve these problems we tried to observe the various effects of electrodeposition parameters on current efficiency. So that we can find out the best plating parameters for good quality plating from  $\text{Cr}^{3+}$  bath. We hope that our findings will contribute to the plating industries for making good quality products.

In this research, we observed the effect of pH, temperature, current density (C.E.) and also time on to the current efficiency. On the other hand we also observed the effect of the concentration of  $\text{CrCl}_3$  on the plating thickness and optical reflectivity.

## 2. EXPERIMENTAL DETAILS

Commercial grade mild steel coupons were used as cathode for chromium plating having dimension 4 cm x 4 cm x 0.05 cm. The coupons were polished successively with different grade of emery paper down to 1200 to obtain a mirror finish surface, washed thoroughly with liquid soap solution, degreased in acetone and finally rinsed in distilled water. The air dried specimen was insulated with synthetic paint leaving 1 cm x 1 cm area exposed for experiment. The electroplating was carried out galvanostatically in an open glass beaker containing the electrolyte with mild steel coupon as cathode and platinum foil as anode connected to a controllable dc power source (GW Instek GPS 3030DD DC Power Supply, USA). The experimental configuration is shown in Fig. 1.

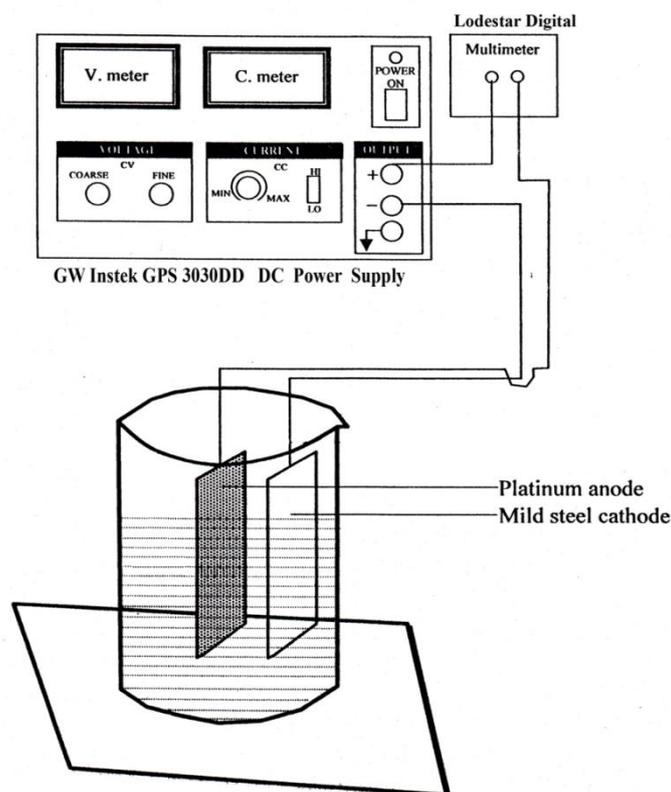


Fig. 1. Schematic cell diagram of chromium (III) plating bath

The electrolyte for trivalent chromium plating was  $\text{CrCl}_3$  as a source of trivalent chromium ion,  $\text{HCOOH}$  as a complexant,  $\text{Na}_2\text{SO}_4$  as a mixed electrolyte system, PEG as an organic additive and  $\text{H}_3\text{BO}_3$  as a buffering agent. All chemicals used were analytical grade reagents procured from E. Merck, Germany, E. Merck India and UNI-CHEM China. After electroplating the coupon was rinsed with distilled water, air dried and finally dried at  $80^\circ\text{C}$  in an oven for 2 hours. Weight of the dry coupon before and after electroplating was measured using a digital analytical balance. The current efficiency and plating thickness of the deposit were calculated by weight gain method. The average thickness of electrodeposited coating was measured from the amount of metal deposited at certain plating condition. The amount of metal deposited was calculated from the difference of weight before and after plating. The thickness of the coating was then calculated by using the following formula-

$$\text{Thickness, } T = \frac{W}{A \times D} \quad (1)$$

Where,

$W$  = Weight of the electrodeposited coating in gm.

$A$  = Area of the plated surface =  $4 \text{ cm}^2$

$D$  = Density of the electrodeposited metal,  $\text{g/cm}^3$

Density of Cr is  $7.14 \text{ g/cm}^3$  [8]

Current efficiency for Cr plating was calculated from the ratio of the amount of metal deposited to the amount of metal to be deposited at a fixed current and fixed time as stated below:

$$\text{Current efficiency, } \eta = \frac{W_1}{W_2} \times 100 \quad (2)$$

Where,

$\eta$  = Current efficiency

$W_1$  = Weight of metal actually deposited,

$W_2$  = Weight of metal to be deposited.

$W_2$  was calculated from Faraday's law of electrolysis according to the following formula.

$$W_2 = Zit \quad (3)$$

Here,

Z = Electrochemical equivalent of the deposited metal in mg/columbs.

i = Applied current in ampere.

t = Plating time in second.

Electrochemical equivalent for Cr obtained from the literature is 0.0898 mg/columb [8].

Optical reflectivity of the electroplated specimen was measured by UV-Visible spectrophotometer (model UV-1650PC, Shimadzu Corporation, Japan) within the wavelength range between 200 nm to 1100 nm.

### 3. RESULTS AND DISCUSSION

The effect of various deposition parameters on current efficiency is illustrated from Figs. 2 to 5. We also observed the effect of the different concentration of CrCl<sub>3</sub> on the plating thickness and optical reflectivity from Figs. 6 and 7 respectively. Different parameters have different influences on current efficiency. As observe, current efficiency grows up with the rise of pH value up to 3 and after that it decreases gradually (Fig. 2.). The reason is that the chemical reaction (4) takes place at the cathode surface. Due to the excessive hydrogen evolution reaction on the cathode surface a significant

increase of pH value occurred. When the pH exceeds 4.5, then a high molecular weight polymer is formed by a series of reactions on the cathode surface. This process is known as olation. The Cr<sup>3+</sup> ions are trapped inside the complex bridge structure of high molecular weight polymer which restricts the Cr<sup>3+</sup> ion to come out for reduction reaction [7]. So the deposits growth is inhibited. At low pH, the current efficiency is also very low due to excessive hydrogen evolution.

Fig. 3. shows that, the deposition rate as well as current efficiency increases with increasing temperature up to 40°C but above 40°C bath temperature the current efficiency decreases dramatically. This is due to the dispersion of Cr<sup>3+</sup> ions in the bath solution. As the temperature increases the dispersion of Cr<sup>3+</sup> ion increases in the bath. Another important thing is that with increasing the bath temperature the pH changes abruptly. So the dispersion of trivalent chromium ions also increases too much. It affects the plating quality as well as the value of current efficiency.

According to the Fig. 4. the current efficiency increases with increasing the deposition time up to 90 min of deposition time. But after 90 min the current efficiency become saturated with increasing plating time. The saturation of current efficiency with increasing deposition time after 90 min is due to increase the pH value above 4 at

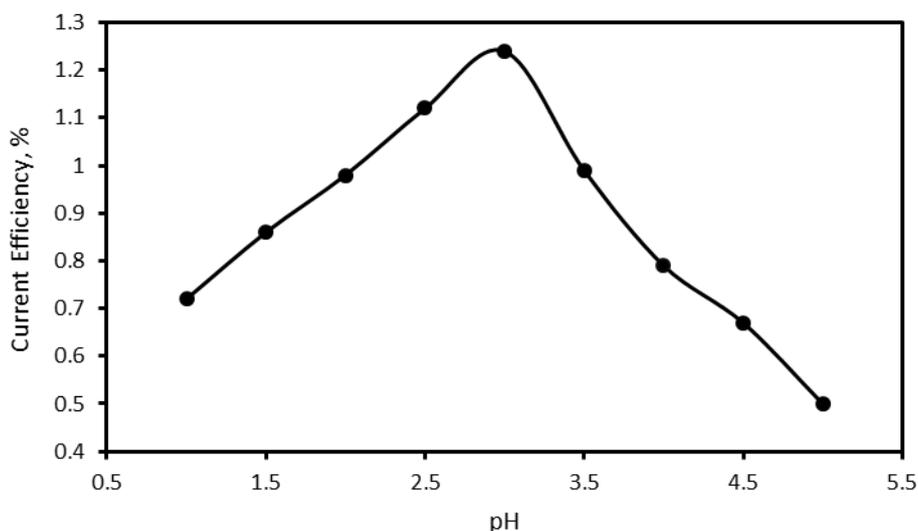
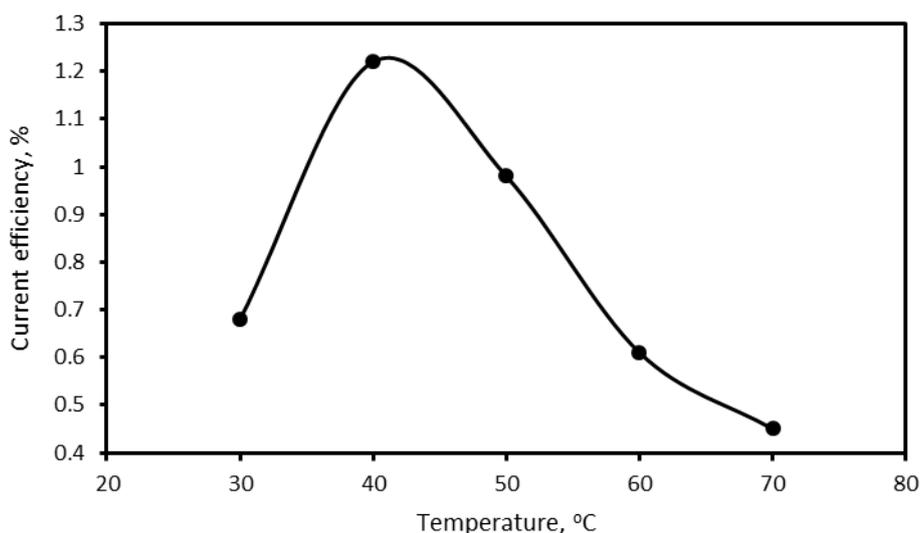
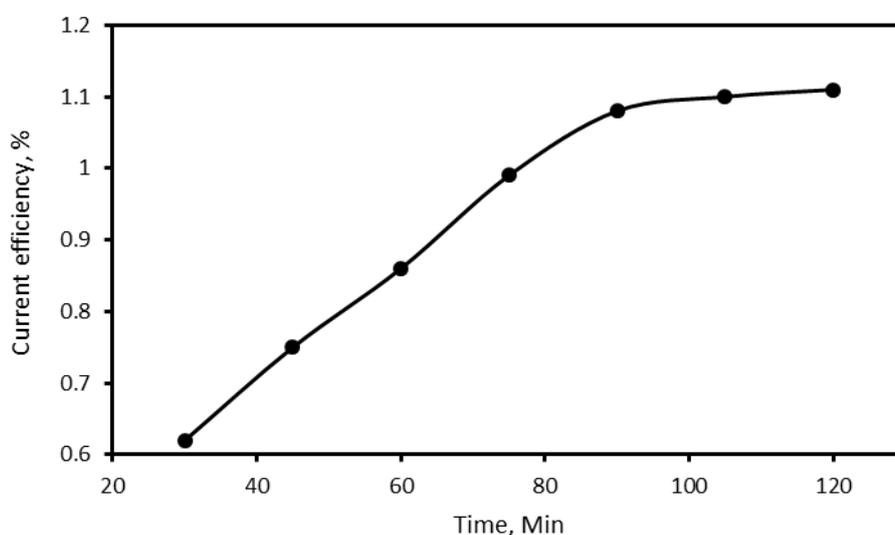


Fig. 2. Current efficiency of the Cr(III) plated mild steel as a function of pH value from the bath containing 110 gram/L CrCl<sub>3</sub>, 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm<sup>2</sup>; deposition time 90 min and temperature 40°C



**Fig. 3. Current efficiency of the Cr(III) plated mild steel as a function of deposition temperature from the bath containing 110 gram/L CrCl<sub>3</sub>, 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm<sup>2</sup>; pH = 3 and deposition time 90 min**



**Fig. 4. Current efficiency of the Cr(III) plated mild steel as a function of deposition time from the bath containing 110 gram/L CrCl<sub>3</sub>, 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm<sup>2</sup>; pH = 3 and temperature 40°C**

the cathode surface and this causes the formation of hexa-aquo complexes which restricts the Cr<sup>3+</sup> ion electro reduction to metal Cr and decrease the deposition rate [9]. That is why the current efficiency become constant after 90 min of deposition time.

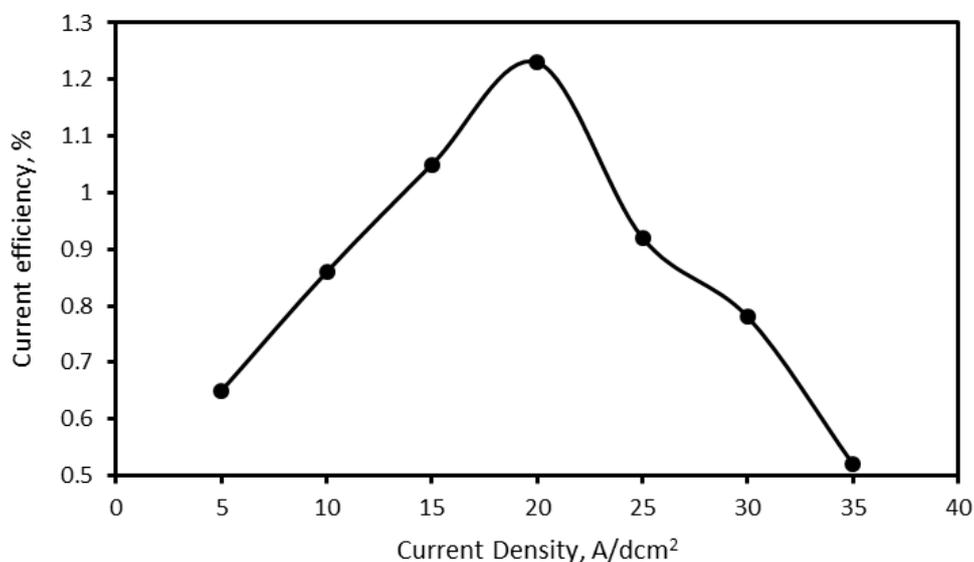
Fig. 5. shows the current density vs current efficiency curve. From this curve, it is clearly shown that, the current efficiency is increased

dramatically up to 20 A/dm<sup>2</sup>, then incrementally declined with raising the current density [10]. The favorable current density for Cr (III) deposition is up to 20 A/dm<sup>2</sup>. At low to moderate current density, the electro reduction of Cr<sup>3+</sup> ions can occur in a regular manner and the deposits are very smooth and stable [10]. But it deteriorates when the current density value exceeds 30 A/dm<sup>2</sup> due to increase the pH at the cathode surface. When the pH is higher, then it

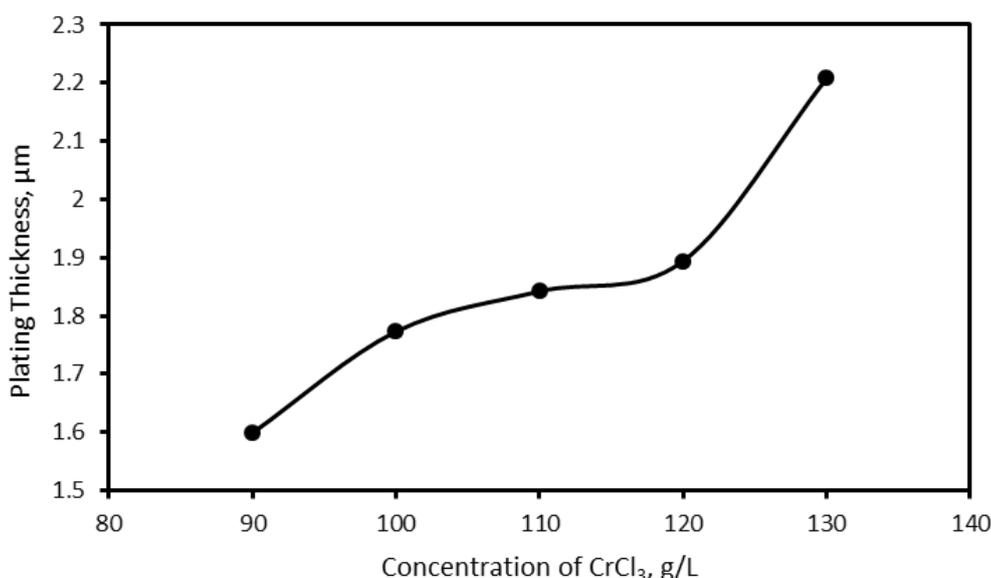
accelerates the formation of high molecular weight complex polymer and also precipitated as chromium hydroxide on to the cathode surface by the reduction process. This precipitates lead to establish irregular, coarse and cracked surface of the deposits [10]. So from our experimental result, we can suggest that, 20 A/dm<sup>2</sup> current density is

the best for achieving comparatively higher current efficiency.

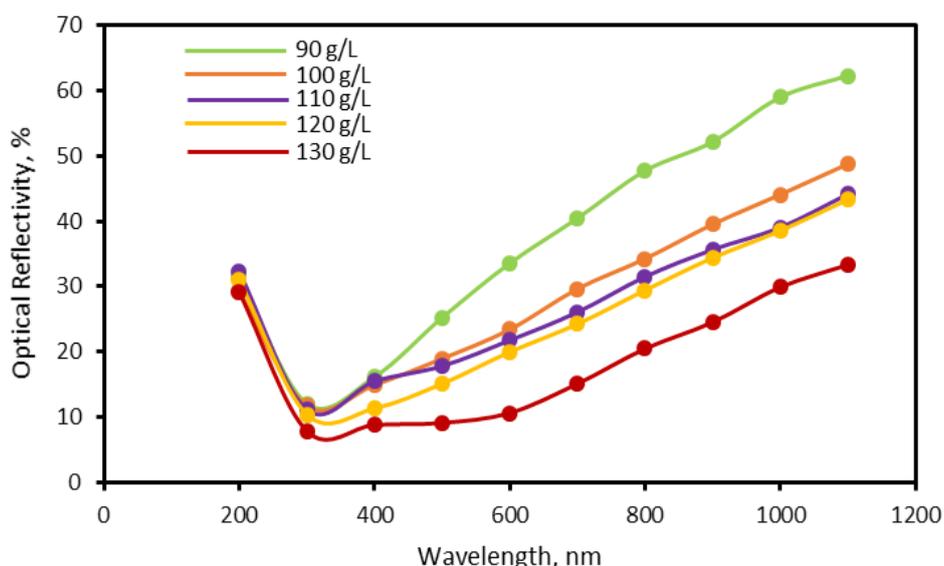
Fig. 6 shows that the thickness of the deposit grows incrementally with raising the concentration of chromium (III) chloride in the bath. Maximum thickness (2.208 μm) was



**Fig. 5.** Current efficiency of the Cr(III) plated mild steel as a function of current density from the bath containing 110 gram/L CrCl<sub>3</sub>, 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: pH = 3, temperature 40°C and plating time 90 min



**Fig. 6.** Plating thickness in terms of chromium (III) chloride concentration from the bath containing 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO and CrCl<sub>3</sub>. Operating conditions: current density 20 amp/dm<sup>2</sup>; temperature 40°C, pH = 3 and plating time 90 min



**Fig. 7. Optical reflectivity of the Cr(III) plated mild steel as a function of wavelength ranging from 200-1100 nm for different chromium tri-chloride concentration from bath containing 40 gram/L Na<sub>2</sub>SO<sub>4</sub>, 40 gram/L H<sub>3</sub>BO<sub>3</sub>, 0.1 gram/L PEG, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm<sup>2</sup>, temperature 40°C, pH = 3 and plating time 90 min**

observed for 130 g/L chromium (III) chloride concentration, the highest concentration of CrCl<sub>3</sub>. There has been a steep increase of thickness after 120 g/L CrCl<sub>3</sub> concentration. This results exhibit that higher concentration of CrCl<sub>3</sub> is beneficial for the thicker chromium (III) plating. This can be explained on the basis of literature report [9] which shows that the kinetics of Cr<sup>3+</sup> electrodeposition is dependent on the limiting current density. The limiting current density again depends on the concentration of Cr<sup>3+</sup> in the solution according to the equation

$$i_L = -FD \left( \frac{C_b - C_s}{\delta} \right)$$

Where,

- $i_L$  = Limiting current
- F = Faraday constant
- D = Diffusion coefficient
- $C_b$  = Concentration of chromium at the bulk
- $C_s$  = Concentration of chromium at the surface
- $\Delta$  = Diffusion layer thickness

When the surface concentration of Cr(III) on the surface becomes zero then the equation becomes-

$$i_L = \frac{-FDC_b}{\delta}$$

Thus, the limiting electrodeposition current is directly proportional to the bulk concentration of the Cr<sup>3+</sup> ion. This explains the increase of current efficiency and plating thickness with increasing the concentration of CrCl<sub>3</sub> in the bath when other parameters remain same. This can also be supported by the experiment of F. A. Lowenheim [11]. He explained that an increase of the concentration of metal salt usually causes the conductivity to approach a maximum for moderate ionic mobility producing an increase of rate of electrodeposition.

Fig. 7. shows the reflectivity as a function of wave length ranging from 200-1100 nm of the chromium (III) plated mild steel at various chromium (III) chloride concentrations. From the figure, it is seen that when the bath contain lower concentration of chromium (III) chloride, the optical reflectivity is very high about 63%. But as the concentration of chromium (III) chloride increases in the bath solution, the optical reflectivity is decreased dramatically. At first, the optical reflectivity decreases in the ultra-violet region at wavelength of 200-300 nm and afterwards the optical reflectivity increases gradually at wavelength of 400-1100 nm (visible and near infrared region). This phenomena is same for all the curves shown in Fig. 7. This is related to the kinetics of the Cr(III) reduction process. In the introduction part, the equation (3) shows the reduction reaction of Cr<sup>3+</sup> ion in the electrolyte. Actually if

the concentration of  $\text{CrCl}_3$  as well as  $\text{Cr}^{3+}$  ion increases in the plating bath then the rate of reduction of  $\text{Cr}^{3+}$  ion increased in the electrolyte and deposit on the mild steel substrate as a metal chromium. But if the concentration of  $\text{Cr}^{3+}$  ion increases gradually in the electrolyte then the rate of reduction is increased abruptly due to having availability of the  $\text{Cr}^{3+}$  ion in the electrolyte. By this way the reduction is dramatically increased and deposit on the substrate surface in irregular manner. So, there is more tendency to form non-uniform surface of plating. Any departure from the brightness is caused by slight irregularities on the surface. Optical reflectivity has direct relationship with the uniformity of plating. More uniform is the surface more is the optical reflectivity. So increasing of  $\text{CrCl}_3$  concentration decreases the optical reflectivity.

#### 4. CONCLUSION

- The highest current efficiency was observed at pH = 3.
- At 40°C temperature, the current efficiency was significantly higher than that any other temperature.
- The optimum plating time was found 90 min due to achieve highest current efficiency.
- 20 A/dcm<sup>2</sup> current density was the best to obtain highest current efficiency.
- The thickness of the deposit grows incrementally with raising the concentration of chromium (III) chloride in the bath but in case of optical reflectivity the result is opposite. Thus with raising the concentration of  $\text{CrCl}_3$  in the bath the optical reflectivity was incrementally declined.

#### 5. ANALYSIS OF ELECTRODEPOSITION

After the whole story, it can be concluded that, the plating thickness was increased with increasing the concentration of  $\text{Cr}^{3+}$  ion in the electrolyte whereas it was opposite in case of optical reflectivity results. But it was also observed that the optimum bath pH, temperature, plating time and current density were 3, 40°C, 90 min and 20 amp/dm<sup>2</sup> respectively. Although we could not obtain good current efficiency, however we can suggest that the above condition is good for Cr(III) electrodeposition. Actually to achieve better current efficiency is very difficult for

trivalent chromium plating due to excessive hydrogen evolution during the experiment and another difficulties is the formation of hexa-aquo complexes on the cathode surface when the pH value reaches above 4. However, we hope that our findings can contribute to the electroplating industries.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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