

Original Research Article**Optimization of the concentration polyethylene glycol (PEG) for the quality trivalent chromium electroplating****Abstract**

The effect of polyethylene glycol (PEG) was observed on the quality of trivalent chromium electroplating. We observed the thickness and the current efficiency of the Cr^{3+} deposit with the varying concentration of PEG molecules in the bath solution. With the increase of PEG concentration, the both parameters were declined. However, the optical reflectivity and the corrosion resistivity increased with increasing concentration of PEG. At 0.3 g/L of PEG in the bath solution, the best quality electrodeposition were observed. We could optimize the PEG concentration for achieving good quality trivalent chromium plating.

Keywords: Trivalent Chromium Electroplating, Polyethylene Glycol, Corrosion, Optical Reflectivity

1. Introduction

Electroplating, deposition of metals from their salt solutions using electricity is the most important method for the production of protective coatings. Electrolytically deposited chromium is used as the outer layer of multilayer protective decorative coating. Two types of electrolytes (chromium source) such as hexavalent and trivalent electrolytes are used in chromium plating. Hexavalent electrolytes are chromic acid, chromic oxide, potassium dichromate etc, and trivalent electrolytes are chromic (III) sulfate, chromic (III) chloride etc. The electrolytes [1] based on hexavalent chromium have good covering properties such as easily deposits on the metal surface, bring bright surface finish, less porous and provides good corrosion resistance. But hexavalent chromium has a long list of serious disadvantages during operating bath solutions. These include low electrochemical equivalent and need to operate at very high current densities, and have low current efficiency combined with high cathodic hydrogen evolution. As chromic [2] acid has a strong oxidizing action on organic substances appropriate protective clothing should be worn when working with it. Chromium (VI) is highly carcinogenic and toxic. Zhang and Li reported the effect of Cr(VI) on the human body such as oral ulcers, diarrhea, abdominal pain, indigestion, vomiting, leukocytosis, and

28 presence of immature neutrophils [3]. According to the report of Saryan and Reedy that some Cr(VI)
29 compounds such as potassium tetra chromate and chromic acid are potent oxidizing agents, and are
30 thus strong irritants of mucosal tissue and also affect the metabolic acidosis, acute tubular necrosis,
31 kidney failure [4]. Mancuso and Hueper investigated that lung cancer associated with chromate
32 production [5]. Polak et al. reveal that Cr(VI) can create severe allergic problem [6]. Cr(VI) is
33 responsible for the respiratory irritations. According to the study of Cohen et al. that nasal ulcers and
34 perforations were associated with total chromium concentrations of 1.4 to 43.9 $\mu\text{g}/\text{m}^3$, averaging 7.1
35 $\mu\text{g}/\text{m}^3$, and Cr(VI) concentrations of 0.09 to 9.1 $\mu\text{g}/\text{m}^3$, averaging 2.9 $\mu\text{g}/\text{m}^3$ [7]. Lindberg and
36 Hedenstierna also found similar effects on nasal pathology and subjective symptoms [8]. The waste
37 disposal from chromium plating industries is another big problem. In developed countries, there are
38 stringent rules against disposal of chromium (VI). Normal treatment of chromium waste effluent
39 involves a reduction of the chromic acid in the still acidified effluent to trivalent chromium and
40 precipitation to the insoluble chromium hydroxide when pH value is adjusted to the range 8-9. The
41 choice of reducing agent for converting hexavalent to the trivalent state depends on several factors,
42 but is largely confined to the use of either ferrous sulfate, sulphurdioxide or sodium metabisulphite.
43 Thus, high toxicity of the chromic acid and mist produced from the bath that involves the need for
44 special precautions to prevent environmental pollution. For these reasons, there has been no
45 shortage of attempts to get away from hexavalent electrolytes. So alternatively, the trivalent chromium
46 is used extensively.

47 For effective trivalent chromium plating, polyethylene glycol (PEG) plays an important
48 role. PEG was used as surfactant in the plating solution that help to achieve good adherence between
49 the electrodeposited metal and substrate [9] Hull cell tests show that the addition of PEG molecules
50 can enhance the homogeneity and the efficiency of current at low current densities and optimum
51 concentration [9]. The effect of PEG is generally understood in terms of its adsorption onto the
52 cathode surface during electrodeposition. In addition, the adsorbed additives block part of the
53 electrode surface, thereby reducing the number of active sites for the formation of nuclei, causing a
54 decline in the nucleation rate [10,11]. Feng et al. [12] studied PEG in copper electroplating and
55 observed that PEG forms a PEG-Cu-Cl complex, which plays a significant role in PEG adsorption to
56 the electrode surface. In the Cu electroplating solution, PEG was completely degraded after 4 h [13].
57 The mechanism of PEG degradation is often explained by complex free-radical and oxidative

reactions accompanied by main C—O bond scission [14,15]. Using various electrochemical methods such as cyclic voltammetry, open circuit potential transition, and electrochemical impedance spectroscopy, Lee et al. [9] studied the effect of PEG on electrochemically deposited trivalent chromium layers. They reported that the presence of PEG molecules results in a low reductive current density and reduces hydrogen evolution reactions through adsorption of PEG onto the electrode surface.

In this work, we investigated the effect of PEG on the chromium deposition through the study of deposits quality. We observed the effect of PEG concentration on the current efficiency, optical reflectivity and corrosion behavior in order to optimize the concentration of this organic surfactant and evaluate the role for quality chromium electrodeposition.

2. Experimental

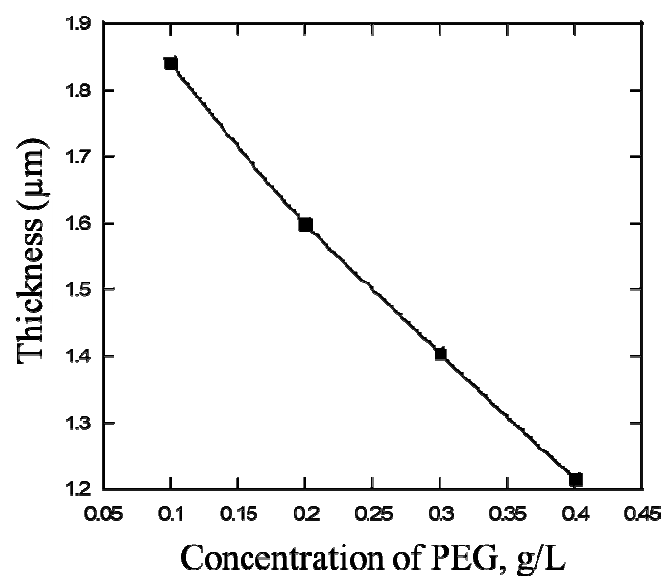
Commercial grade mild steel coupons having dimension 4cm×4cm×0.05cm were used as cathode for chromium plating. The coupons were polished successively with different grade of emery paper down to 1200 to obtain a mirror finish surface, washed thoroughly with soap solution, degreased in acetone and finally rinsed in distilled water. The specimens were dried in air and then insulated with synthetic paint leaving 1cm×1cm area exposed for chromium deposition. The experimental setup was discussed elsewhere [16] The electrolyte for trivalent chromium plating was composed of CrCl_3 as a source of trivalent chromium ion, HCOOH as a complexant, H_3BO_3 as a buffering agent, Na_2SO_4 as a mixed electrolyte system, and PEG as an organic additive. All chemicals used were analytical grade reagents procured from E. Merck Germany, E. Merck India and UNICHEM China. After electroplating the coupon was rinsed with distilled water, air dried and finally dried at 80°C in an oven for 2 hours. Weight of the dry coupon before and after electroplating was measured using a sophisticated digital analytical balance. The calculation of the thickness and current efficiency of the deposit was discussed in our previous article [16]. 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. The computer controlled Wonatech WPG100e Potentiostat was used for the corrosion experiment. The chromium deposited sample was emerged into the simulated cooling water and the Ag/AgCl

reference electrode was placed into the solution and its lagen probe was placed near to the tested sample. In the cell preparation the counter electrode (platinum foil), the reference electrode (Ag/AgCl) and the working electrode (trivalent chromium plated mild steel) were placed parallely into the electrolyte and by the potentiodynamic method the corrosion behavior of the Cr(III) plated mild steel were observed. In the potentiodynamic method, the current and voltage value were changed continuously and the chemical reaction proceed between the Cr (III) plated sample on the exposed area and the electrolyte due to set a range of voltage from -0.5V to +1.0V. The sweep rate was 0.5 mV/sec, and the sweep was continued until the anodic current reached approximately 10 mA. The corrosion behavior was displayed on the computer screen by means of the graphical presentation.

3. Results and Discussion

3.1 The effect of polyethylene glycol (PEG) concentration on the plating thickness and current efficiency

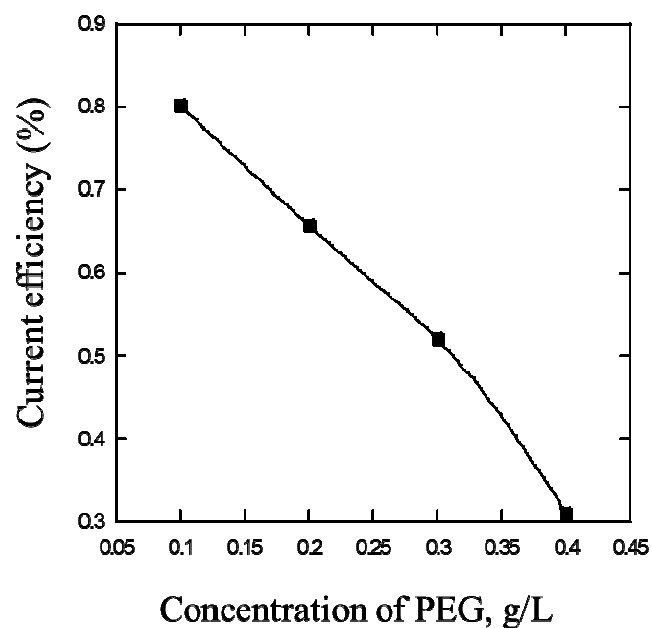
The effect of polyethylene glycol (PEG) on the thickness for chromium plating on the mild steel was investigated from the bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , and 4 ml/L HCHO with constant agitation. The applied current density, plating time and bath temperature were 20 amp/dm², 2 hours and 40°C, respectively, during plating. As shown in Fig. 3.1.1 that the plating thickness linearly decreased with the increase of polyethylene glycol (PEG) concentration. The maximum thickness (1.842μm) was observed with 0.1 g/L of PEG concentrations. On the other hand, the current efficiency linearly decreased with the increase of polyethylene glycol (PEG) concentration shown in Fig. 3.1.2. The maximum current efficiency (0.802%) is observed for 0.1 g/L polyethylene glycol concentration. These graphs show that lower concentration of PEG is beneficial to obtain higher plating thickness current efficiency.



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112 **Fig 3.1.1.** Plating thickness as a function of polyethylene glycol (PEG) concentration from the bath
 113 containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , 4 ml/L HCHO and PEG.
 114 Operating conditions: Current density 20 amp/dm²; temperature 40⁰ C and plating time 2 hours.

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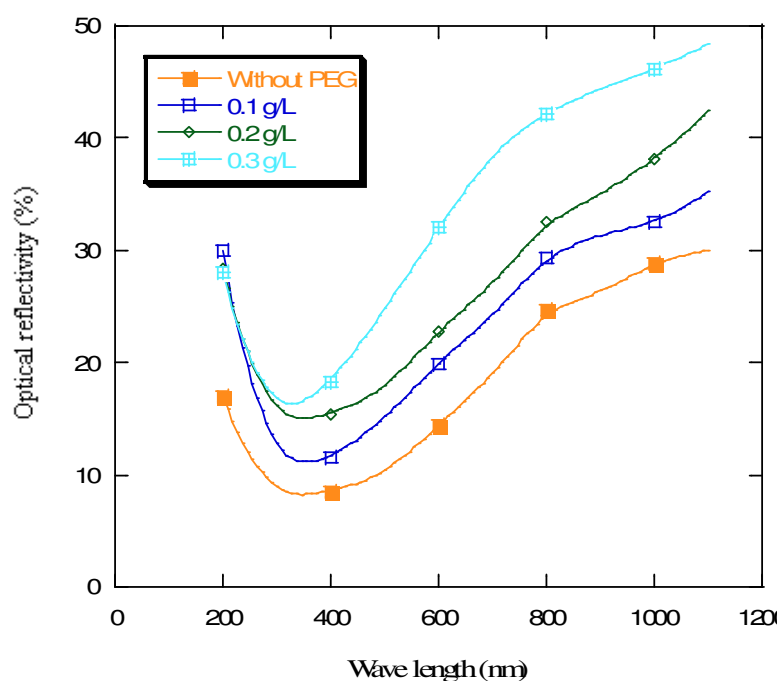
117 **Fig 3.1.2.** Current efficiency of the Cr(III) plated mild steel as a function of polyethylene glycol (PEG)
 118 concentration from the bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH ,

119 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm²; temperature 40⁰ C and plating time
120 2 hours.

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122 3.2 The effect of polyethylene glycol (PEG) concentration on the optical reflectivity

123 Fig. 3.2.1 shows the reflectivity as a function of wave length ranging from 200-1100 nm of the
124 chromium (III) plated mild steel at various polyethylene glycol concentrations and the bath containing
125 110 g/L chromium (III) chloride (CrCl₃), 40 g/L sodium sulfate (Na₂SO₄), 40 g/L boric acid (H₃BO₃), 40
126 ml/L formic acid (HCOOH), 4 ml/L formaldehyde (HCHO). Operating conditions: current density 20
127 amp/dm², temperature 40⁰ C and plating time 2 hours. As indicated from the figure, it is seen that the
128 Cr (III) plated surfaces obtained from the solution containing 0.3 g/L polyethylene glycol reflect much
129 light for all wavelengths ranging from 200-1100 nm as compared to other polyethylene glycol
130 concentrations. The maximum optical reflectivity was 48.4% for 0.3 g/L polyethylene glycol and the
131 minimum optical reflectivity (30.02%) was observed for the electrolyte containing zero polyethylene
132 glycol concentrations. At first, in the UV region the optical reflectivity was decreased. Afterwards the
133 optical reflectivity increases rapidly up to 800 nm wavelengths (visible region) and increased slowly up
134 to 1100 nm wavelengths (near infrared region) for all concentrations of the polyethylene glycol (PEG).



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Fig 3.2.1. Optical reflectivity of the Cr(III) plated mild steel as a function of wavelength for different polyethylene glycol (PEG) concentration from bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , 4 ml/L HCHO . Operating conditions: Current density 20 amp/dm^2 , temperature 40⁰ C and plating time 2 hours.

3.3 The effect of PEG concentration on the corrosion characteristics

Anodic potentiodynamic sweep experiments were conducted to see the effect of polyethylene glycol (PEG) concentration on the corrosion behavior for chromium plated mild steel from the bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , 4 ml/L HCHO and 0.1 g/L, 0.2 g/L, 0.3 g/L PEG. The applied current density, bath temperature and plating time were current density 20 amp/dm^2 , temperature 40⁰ C and plating time 2 hours, respectively, during plating. All sweeps were started at the open circuit potential (corrosion potential) after one hour immersion of the plated steel in simulated cooling water (SCW) for conditioning. The sweep rate was 0.5 mV/sec, and the sweep was continued until the anodic current reached approximately 10 mA. Fig. 3.3.1 shows the relationship between the $\log i$ and applied potential in volt wrt. saturated Ag/AgCl electrode. For all three concentrations of PEG the current increased with the increase of applied anodic potential. However, current increased more rapidly with applied potential when plating was made from bath containing 0.2 g/L PEG. The current increase was least rapid for mild steel plated from bath containing 0.3 g/L PEG. In case of 0.1 g/L PEG, there have been a sudden jump of current after certain potential. This type of current jump is an indication of surface breakdown. In this case, this surface breakdown is an indication of exfoliation of chromium plating from the steel substrate. The surface breakdown occurred at more negative potential (approximately -0.41V) for 0.1 g/L PEG. The results show that mild steel plated from bath containing 0.3 g/L PEG is most corrosion resistive and that plated from 0.2 g/L PEG is least corrosion resistive among the three concentrations PEG. This is due to the formation of smooth, uniform and compact deposition of chromium on the mild steel substrate when 0.3 g/L PEG was used in the bath constituents.

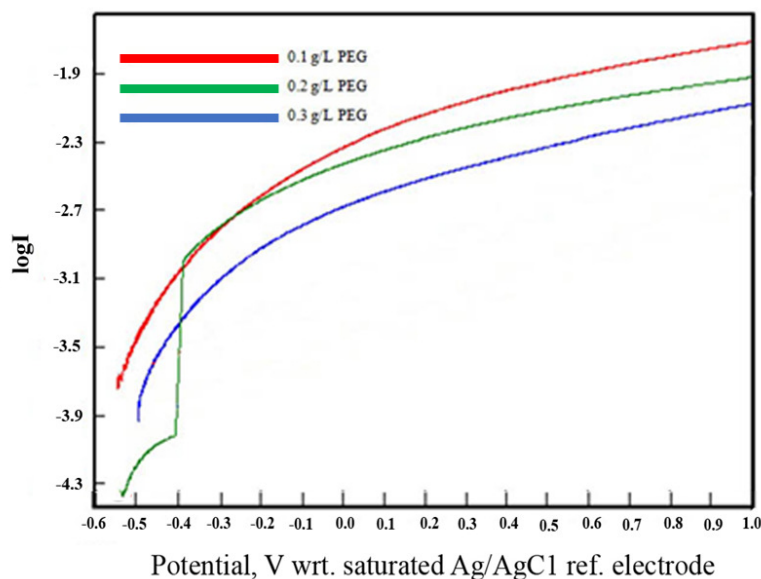


Fig 3.3.1. Corrosion behavior of the Cr(III) plated mild steel as a function of polyethylene glycol (PEG) concentration from the bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , 4 ml/L HCHO . Plating conditions: Current density 20 amp/dm²; temperature 40⁰ C and plating time 2 hours. Test medium: SCW; immersion period, 1 hour and sweep rate, 0.5 mV/sec.

3.4 Discussion

The role of PEG is significant for chromium plating. PEG absorbed on the active sites and blocked the area. However, the chromium deposited on the less active sites and uniform and smoother deposition resulted [17]. Therefore, if the concentration increased in the bath of chromium plating, the more active sites blocked and that produced quality plating with finer grains and high compactness [18], as we discussed in our previous article [19]. Lee *et al.* also found the relation between concentration of PEG and film quality and stated that the compact and smooth film can be obtained at higher PEG concentration [9]. From the above discussion, it is clear that the plating thickness and current efficiency decreased with the increased of PEG concentration. For the same reason, the best optical reflectivity was observed from the higher concentration of PEG containing in the bath solution. As the deposits was very uniform and compacted at higher concentration of PEG, so at the 0.3 g/L PEG concentration, the chromium deposits on the mild steel substrate was most

corrosion resistive according to our observation among the three bath concentrations used in this corrosion experiment.

4. Conclusion

The effect of concentration of PEG in the bath solution on the chromium electroplating was observed in this current research. The plating thickness and current efficiency were decreased and optical reflectivity was increased with the increase of PEG concentration in the bath solution. The concentration of 0.3 g/L PEG exhibited the highest optical reflectivity and corrosion resistivity. So higher concentration of PEG in the bath solution is beneficial to obtain good quality chromium electrodeposition on the mild steel substrate.

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