

Role of polyethylene glycol (PEG) on trivalent chromium electrodeposition

Abstract

The effect of polyethylene glycol (PEG) was observed on the quality of trivalent chromium electroplating. The thickness and the current efficiency of the Cr^{3+} deposit were decreased with increasing the concentration of PEG, whereas the optical reflectivity and the corrosion resistivity increased. At the higher concentration of PEG (0.3 g/L), the best quality electrodeposition was observed.

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

1. Introduction

Electroplating is a method of depositing metals on a substrate from their salt solutions using electricity. Electrolytically deposited chromium can be used as multilayer protective 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 based on hexavalent chromium exhibits good covering properties and provides good corrosion resistivity [1]. But hexavalent chromium consists of a long list of serious disadvantages during the operation of deposition including low electrochemical equivalency and very high operating current densities and have low current efficiency combined with high cathodic hydrogen evolution. Chromium (VI) is highly carcinogenic and toxic [2]. Zhang and Li reported the effect of Cr(VI) on the human body such as oral ulcers, diarrhea, abdominal pain, indigestion, vomiting, leukocytosis, and presence of immature neutrophils [3]. According to the report of Saryan and Reedy, some Cr(VI) compounds such as potassium tetra chromates and chromic acids are potential oxidizing agents, and act as a strong irritants of mucosal tissue and also responsible for affecting the metabolic acidosis, acute tubular necrosis, kidney disease [4]. Mancuso and Hueper investigated that lung cancer may occur due to the chromate production [5]. Polak et al. reveal that Cr(VI) can create severe allergic problem [6]. Cr(VI) is

28 responsible for the respiratory irritations. According to the study of Cohen et al., nasal ulcers and
29 perforation arises when the chromium concentrations are ranging from 1.4 to 43.9 $\mu\text{g}/\text{m}^3$ [7]. Lindberg
30 and Hedenstierna also found similar effects on nasal pathology and subjective symptoms [8]. The
31 waste disposal from chromium plating industries is another big problem. In developed countries, there
32 are stringent rules against disposal of chromium (VI). Normal treatment of chromium waste effluent
33 involves a reduction of the chromic acid in the acidified effluent to trivalent chromium and precipitation
34 to the insoluble chromium hydroxide when pH value adjusted to the range of 8-9. The choice of
35 reducing agent for converting hexavalent to the trivalent state depends on several factors but is
36 largely confined to the use of either ferrous sulfate, sulphur dioxide or sodium metabisulphite. Thus,
37 high toxicity of the chromic acid and mist produced from the bath that involves special precautions to
38 prevent environmental pollution. For these reasons, there has been no shortage of attempts to get
39 away from hexavalent electrolytes. So alternatively, the trivalent chromium is used extensively.

40 For effective trivalent chromium plating, polyethylene glycol (PEG) plays an important
41 role. PEG was used as surfactant in the plating solution that helps to achieve good adherence
42 between the electrodeposited metal and substrate [9] Hull cell tests show that the addition of PEG
43 molecules can enhance the homogeneity and the efficiency of current when using low current
44 densities and optimum concentration [9]. The effect of PEG is understandable in terms of its
45 adsorption onto the cathode surface during electrodeposition. In addition, the adsorbed additives act
46 to block part of the electrode surface, thereby reducing the number of active sites for the formation of
47 nuclei which is the main cause for decreasing the nucleation rate [10,11]. Feng et al. [12] studied the
48 effect of PEG on copper electroplating and observed that PEG forms a PEG–Cu–Cl complex, which
49 plays a significant role by adsorbing PEG on the electrode surface. In the Cu electroplating solution,
50 PEG was degraded completely after 4 hours [13]. The mechanism of PEG degradation is explained
51 by complex free-radical and oxidative reactions accompanied by main C—O bond scission [14,15].
52 Many researchers studied the electrochemical effect of chromium deposits using various
53 electrochemical methods such as cyclic voltammetry, open circuit potential transition, and
54 electrochemical impedance spectroscopy. Lee et al. [9] studied the effect of PEG on electrochemically
55 deposited trivalent chromium layers. They reported that the presence of PEG molecules results in a
56 low reductive current density and reduces often hydrogen evolution reactions through adsorption of
57 PEG onto the electrode surface.

In this work, we investigated both the mechanical and electrochemical effect of PEG on the trivalent chromium deposits. We observed the variation of thickness, current efficiency, optical reflectivity and corrosion resistivity as a function of varying PEG concentration in order to optimize the concentration of this organic surfactant.

2. Experimental

Commercial grade mild steel coupons having dimension 4cm×4cm×0.05cm were used as cathode for trivalent chromium plating. The coupons were polished successively with different grade of emery paper down to 1200 to obtain a mirror polished 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. The 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 specimens were measured by UV-Visible spectrophotometer (model UV-1650PC, Shimadzu Corporation, Japan) at the wavelength range of 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 lagon 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 parallelly 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 values were changed continuously and the chemical reaction proceeds 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.

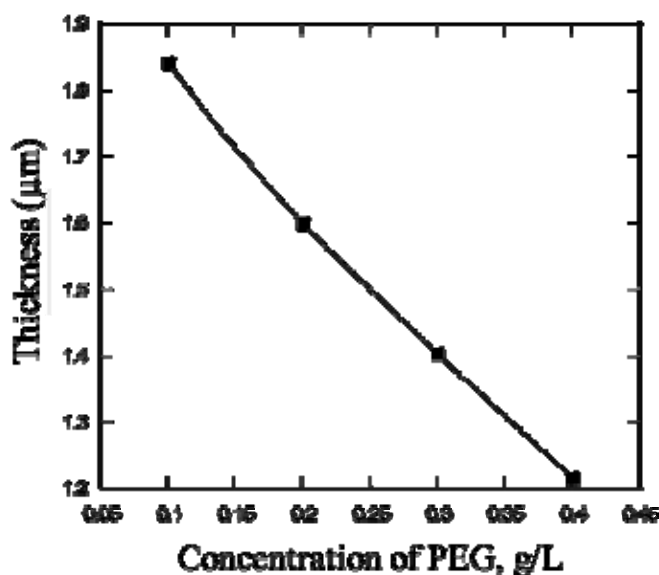
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3. Results and Discussion

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 surface 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 increasing the concentration of polyethylene glycol (PEG). The maximum thickness (1.842μm) was observed at 0.1 g/L of PEG concentrations. Similarly, the current efficiency linearly decreased with increasing the concentration of polyethylene glycol (PEG) shown in Fig. 3.1.2. The maximum current efficiency (0.802%) was observed for lower concentration of polyethylene glycol. These graphs show that lower concentration of PEG is beneficial to obtain desirable plating thickness and current efficiency.

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Fig 3.1.1. Plating thickness 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 and PEG. Operating conditions: Current density 20 amp/dm^2 ; temperature 40°C and plating time 2 hours.

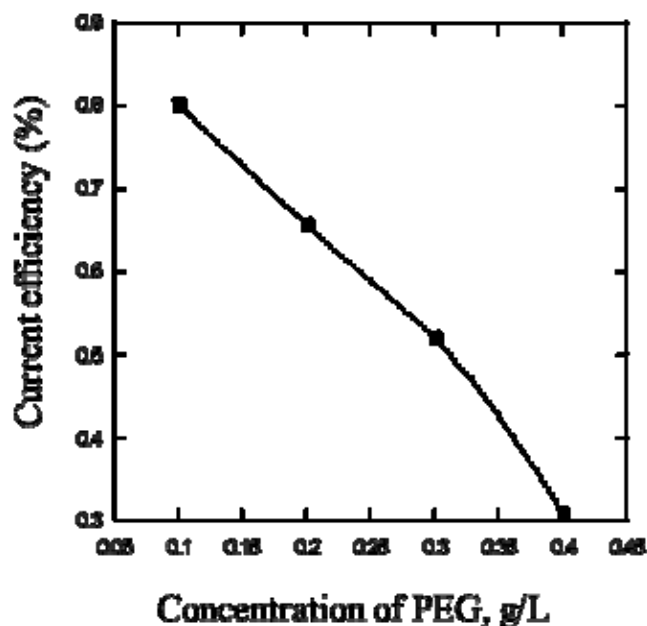


Fig 3.1.2. Current efficiency of the Cr(III) plated mild steel as a function of polyethylene glycol (PEG) concentration from the bath containing 110 g/L CrCl_3 , 40 g/L Na_2SO_4 , 40 g/L H_3BO_3 , 40 ml/L HCOOH , 4 ml/L HCHO . Operating conditions: Current density 20 amp/dm^2 ; temperature 40°C and plating time 2 hours.

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

Fig. 3.2.1 shows the reflectivity as a function of wavelength ranging from 200-1100 nm of the chromium (III) plated mild steel at various concentrations of polyethylene glycol. The bath solution contains 110 g/L chromium (III) chloride (CrCl_3), 40 g/L sodium sulfate (Na_2SO_4), 40 g/L boric acid (H_3BO_3), 40 ml/L formic acid (HCOOH), 4 ml/L formaldehyde (HCHO). Operating conditions were fixed as current density 20 amp/dm^2 , temperature 40°C and plating time 2 hours. As indicated in Fig. 3.2.1, the electrolyte contains 0.3 g/L polyethylene glycol reflect much light for almost all wavelengths

ranging from 200-1100 nm as compared to other concentrations of polyethylene glycol. The maximum optical reflectivity was found 48.4% for 0.3 g/L polyethylene glycol and the minimum optical reflectivity (30.02%) was observed for the electrolyte without containing any polyethylene glycol in solution. In the UV region, the optical reflectivity was sharply decreased and afterwards the optical reflectivity increases rapidly up to 1100 nm wavelengths visible and near-infrared region for all concentrations of the polyethylene glycol (PEG) used in this case.

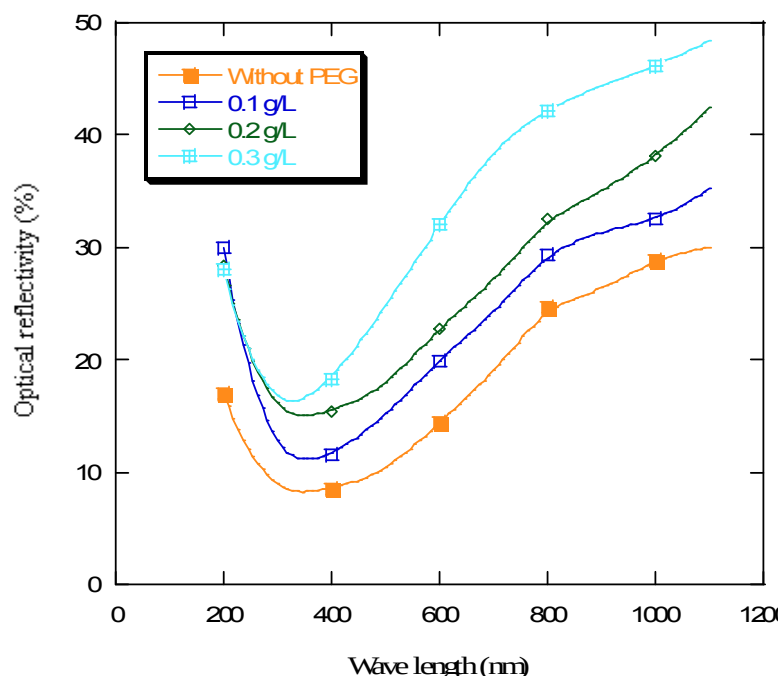


Fig 3.2.1. Optical reflectivity of the Cr(III) plated mild steel as a function of wavelength for different polyethylene glycol (PEG) concentration from bath containing 110 g/L CrCl₃, 40 g/L Na₂SO₄, 40 g/L H₃BO₃, 40 ml/L HCOOH, 4 ml/L HCHO. Operating conditions: Current density 20 amp/dm², temperature 40^o C and plating time 2 hours.

3.3 The effect of PEG concentration on the corrosion characteristics

Anodic potentiodynamic sweep experiments were conducted to observe the effect of polyethylene glycol (PEG) concentration on the corrosion behavior of chromium plated mild steel from the bath containing 110 g/L CrCl₃, 40 g/L Na₂SO₄, 40 g/L H₃BO₃, 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/dm², 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 current (log I) and applied potential in volt with respect to the 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 0.1 g/L PEG. The current was increased slowly 0.3 g/L PEG compared to the other concentrations. In case of 0.2 g/L PEG, there has 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 when the trivalent chromium bath contains 0.3 g/L PEG, then the plated sample exhibits most corrosion resistivity. Whereas the plating bath containing 0.2 g/L PEG reveal least corrosion resistivity. We observed the formation of smooth, uniform and compact deposition of trivalent chromium on the mild steel substrate when 0.3 g/L PEG used into the bath constituents.

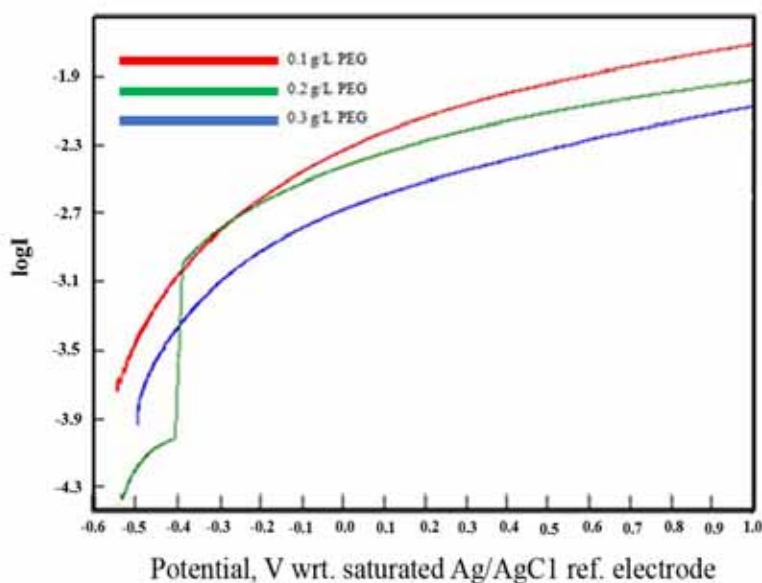


Fig 3.3.1. Corrosion behavior of the Cr(III) plated mild steel as a function of polyethylene glycol (PEG) concentration from the bath containing 110 g/L CrCl₃, 40 g/L Na₂SO₄, 40 g/L H₃BO₃, 40 ml/L HCOOH, 4 ml/L HCHO. Plating conditions: Current density 20 amp/dm²; temperature 40 °C and plating time 2 hours. Test medium: SCW; immersion period, 1 hour and sweep rate, 0.5 mV/sec.

3.4 Discussion

The role of PEG is vital for trivalent chromium plating. PEG adsorbed on to the active sites and blocked the area. However, the chromium deposited on the less active sites and thus uniform and smoother deposition resulted [17]. Therefore, if the concentration increases in the bath, 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 the concentration of PEG and film quality and stated that the compact and smooth film could be obtained at higher PEG concentration in the bath solution [9]. We observed that, at higher concentration of PEG, the plating thickness and current efficiency were decreased whereas optical reflectivity and corrosion resistivity were increased which is consistent with the findings of other researchers. As the deposits were uniform and compacted at higher concentration of PEG, therefore, the chromium deposits on the mild steel substrate exhibited the highest level of corrosion resistivity according to our observation among the three concentrations of PEG that used in this work.

4. Conclusion

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

185 **References**

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