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# Performance Characteristics of Corrosion Resistant Black Coatings

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## Abstract

A new trivalent chromium black plating based on trivalent chromium and cobalt metal has been optimized both in the as plated as well as annealed conditions. The annealed coatings exhibited high hardness, good corrosion resistance and optical properties. XRD and SEM investigations confirmed the formation of intermetallic phases of Cr-Co-P which induced mechanical properties of the coatings. The corrosion resistance characteristics of coatings have been evaluated in 3.5% NaCl using potentiodynamic polarization and A.C impedance measurements. The black coatings offered a good absorption and emission properties.

*Keywords*: trivalent; black; corrosion; optical.

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**Nomenclature**

| | |
|---|---|
| A/E | absorption/emissivity |
| n | surface uniformity |
| $R_t$ | charge transfer resistance |
| $C_{dl}$ | double layer capacitance |
| A | absorption |
| R | reflectance |
| XRD | X-ray diffraction |
| SEM | scanning electron microscope |
| V.H.N | vickers hardness number |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | absorptivity |
| $\varepsilon$ | emissivity |
| $\tau$ | relaxation time |
| $\mu$ | rate of deposition |

*Subscripts*

| | |
|---|---|
| *corr* | corrosion |
| *CPE* | constant phase equivalent |

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## 1. Introduction

Hexavalent chromium coatings are commonly used in industrial practice due to their high hardness, admirable wear resistance and corrosion resistance. Owing to the high toxic in nature, the usage of hexavalent chromates has been limited resulting to develop alternative surface coatings for hard and decorative chromium coatings [1-3]. Patel et al.,[4] and Monteiro [5] reported the development of less-toxic trivalent chromium coatings which plays a vital role in terms of environmental concerns. Also the development of black coatings deserves much attention owing to its optical properties for solar thermal collectors. An ideal solar collector surface has an absorptivity ($\alpha$) that is high at low wavelengths in order to capture the solar irradiation and an emissivity ($\varepsilon$) that is low at high wavelengths in order to minimize radiation heat loss. So developments of selective surfaces are important for achieving high collector efficiency.

Recently G. Li and his co researchers [6] and Gabe et al., [7] have developed trivalent black coatings for achieving good optical properties. The investigations on trivalent black coatings have been made by Zeinab [8] based on Sodium dihydrogen phosphate. Even though the reported trivalent black coatings offered better A/E ratio (the ratio between its absorption of solar radiation and its infrared emission), some of them have not exhibited corrosion resistance properties. The detailed analysis of literature preambled that no considerable reports are available for the corrosion resistance performance of trivalent black chromium coatings. In this paper, we have attempted for obtaining good corrosion resistance black coatings by electrodeposition with high A/E ratio employing trivalent chromium bath. The corrosion potential and corrosion current values were calculated from Potentiodynamic polarization. Electrochemical Impedance Spectroscopy (EIS) measurements was carried out by measuring parameters like relaxation time ($\tau$) and surface uniformity (n) with addition to charge transfer resistance ($R_t$) and double layer capacitance ($C_{dl}$) to validate the enhanced corrosion resistance of annealed coatings at $300^0$C. Also, the use of sodium fluoride is recommended instead of hexafluorosilicic acid which is less toxic and inexpensive. The present work aims to a trivalent black chromium coating with low toxic and inexpensive which can also exhibit both high A/E ratio and better corrosion resistant for Ni composites.

## 2. Experimental

The composition of the bath is given as: $CrCl_3.6H_2O$-263 g.l$^{-1}$; $CoSO_4$-15 g.l$^{-1}$; $Co(NO_3)_2$-12 g.l$^{-1}$; $NaH_2PO_4$-6 g.l$^{-1}$; NaF-20 g.l$^{-1}$; Anode: Lead; Temperature-34 $^o$C; pH-Solution pH; Current density-0.4 A.cm$^{-2}$; Time-5 minutes.

In this study, the influence of Sodium fluoride was analyzed which is a replacement for hexafluorosilicic acid. The addition of NaF favours the uniformity of black coatings. The co-deposition of cobalt enhanced the intensity of the black colour in the coating. The addition of cobalt [9-10] improved the corrosion resistance and optical properties of trivalent chrome black coatings. The nitrate ions of cobalt further facilitated blackening effect to the coating. Hence, the resultant trivalent black chrome coatings were highly intensive in black colour. Trivalent chromium has a remarkable property of forming various types of complexes in aqueous media [11]. It is imperative to utilize weak complexing ingredients to prevent formation of unexpected complexes. Hence, sodium dihydrogen phosphate was used as weak complexing agent [12]. Optical properties, viz., absorption and emittance were measured by UV-VIS spectra as described elsewhere [13].

It has been well established fact that the absorption values of black coatings can be calculated using Kirchhoff's equation [14] A + R = 1 (for black surfaces, transmittance is nil). The potentiodynamic polarization and A.C impedance measurements were carried out in EG&G Princeton Applied Research: Model 7310, Potentiostat – Galavanostat. The scan rate was 1 mV.sec$^{-1}$. The working electrode was 1 cm$^2$ trivalent chrome coated steel. The auxiliary and reference electrodes used were of 4 cm$^2$ area of platinum foil and $Hg/Hg_2Cl_2$/3.5% NaCl. The surface morphology of the coatings was analyzed by XRD and SEM. The Debye–Scherrer equation was used to determine the particle sizes. XRD patterns were recorded in a Philips PW 3710(Cu $K_\alpha$ radiation with wavelength 1.5406 Å, scan rate 1 degree per minute). Scanning Electron Microscopy of the samples was carried out on Philips XL 30 with developed coatings to estimate the surface characteristics of the sample. The hardness of coatings was tested using Vicker's micro hardness tester with an indentations of 100 g load both in the as plated as well as annealed conditions. The absorbance, emittance and A/E ratio were measured using Shimadzu-UV-Vis spectra. The thickness and compositions of the coatings were studied by eddy current tester and then compared with weight gain studies.

## 3. Results and Discussion

### *3.1 Weight gain studies*

The results of black coatings obtained in the present study by weight gain method are presented in Table 1.

$$\text{Rate of deposition } (\mu) = \left[\frac{\text{Weight gain (in grams)} \times 10^{-4}}{\text{Density of Cr}^{3+}}\right] \times \text{Area} \times \text{time} \qquad \text{(in minutes)}$$

The thickness of the optimized coatings obtained was 31µm and the plating time was 7 minutes. This study indicates that a grayish black deposit was obtained at 1 minute and intensive black coatings were observed at 7th minutes. Beyond 7th minutes, the deposit was found as matt due to the collisions among the moving particles impeded the deposition process in the plating bath. Table 1 indicates the coating thickness measured using Eddy current tester at various deposition timings. From the table, it is observed that the coating thickness is increased with deposition time up to 7th minute and afterwards due to matt deposition it is not coated on the substrate.

Table 1. The results of weight gain studies for black coatings

| S.No. | Coating | Deposition timings (min.) | Thickness (µm) | Colour of coatings |
|---|---|---|---|---|
| 1 | Trivalent Cr | 1 | 6.7 | Grayish black |
| 2 | Trivalent Cr | 5 | 12.7 | Semi black |
| 3 | Trivalent Cr | 7 | 31 | Intensive black |
| 4 | Trivalent Cr | 10 | Matt deposits | Matt deposits |

### 3.2 Hardness measurements

The hardness of the electrodeposited trivalent coatings measured by Vicker's hardness tester is given in Table 2. The higher hardness of trivalent black Cr coatings can be attributed to the formation of uniform metallic layers in the coatings. The increased hardness values for black coatings after annealing at 300 °C is due to the precipitation of intermetallic phases of trivalent chromium, Co-P and Cr-Co constituents. Beyond 400°C, a decreased trend in hardness was noticed due to the removal of coating layers at that temperature which is confirmed by the SEM image shown in figure 3(c).

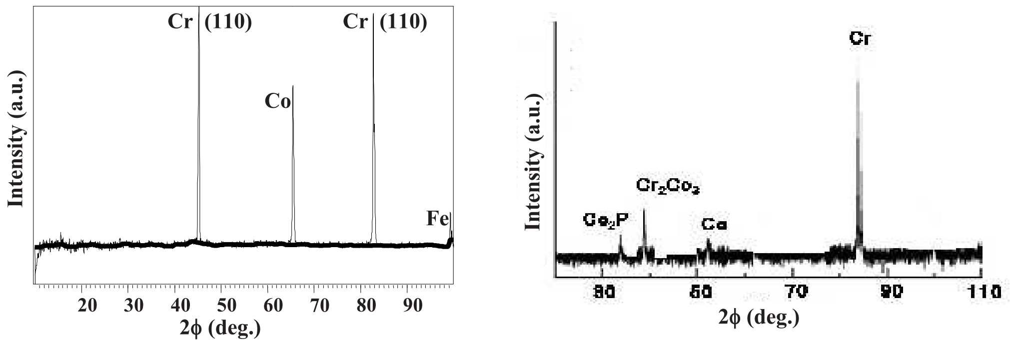
Table 2. Hardness measurements for Trivalent black chromium coatings

| S.No | Coatings | Hardness (V.H.N) Load:100g | | |
|---|---|---|---|---|
| | | As plated | Annealed at 300°C | Annealed at 400°C |
| 1 | Trivalent Cr coatings | 380 | 460 | 452 |

### 3.3 Surface morphology of the black coatings

#### 3.3.1 X-ray diffraction analysis

The results of XRD analysis for trivalent chromium based black coatings in as plated condition is shown in figure 1(a). The crystalline peaks are resulted from the nickel and alloys. A sharp dominant peaks appearing around 2Ǿ values of 45.23 and 82.71confirm the existence of trivalent chromium (110 lattice plane) in the black coatings. The short peaks at 2Ǿ values of 65.46 and 99.27 correspond to the presence of cobalt metal in the black coatings which results in the highest hardness of black coatings than mild steel substrate. Figure 1(b) shows the XRD data for black chromium coatings annealed at 300 °C. It is possible to detect the existence of trivalent chromium at (2Ǿ values of 84.3) 110 plane. The thin peaks at 2Ǿ values of 32.4, 37.6 and 51.9 confirm the presence of cobalt (200 plane) in the coatings as an intermetallic precipitate. The formation of intermetallic phases like Cr-Co, Co-P by precipitation hardening of coatings after annealing at 300 °C enhanced the corrosion resistance and optical properties of the coatings. At 400 °C, the coatings layer began to worn out which is liable for poor corrosion resistance.



(a) (b)

Fig. 1. XRD for trivalent black chromium coatings in (a) as plated condition and (b) after annealing at 300°C.

### 3.3.2 Scanning Electron Microscopic studies

Figure 3(a) shows the SEM images of black coatings obtained from trivalent chrome bath. It can be found that the morphology changes remarkably. For the trivalent black coatings (figure 2a), the high uniformity and compactness is visible. In the case of annealed surface at 300°C, the layered, dense, less dendrite and close packing of atoms with regular arrangement of particles can be seen in figure 2(b). This could be the reason for enhanced corrosion resistance of the black coatings. SEM image (figure 2c) for annealed steel coated with trivalent chromium at 400°C, indicates the compact and non uniformity of atoms resulted by peeling off coatings at that temperature. This indicates that the present coatings cannot be used above 400°C. These results are in good agreement with surface in homogeneity values (n) calculated from impedance measurements.

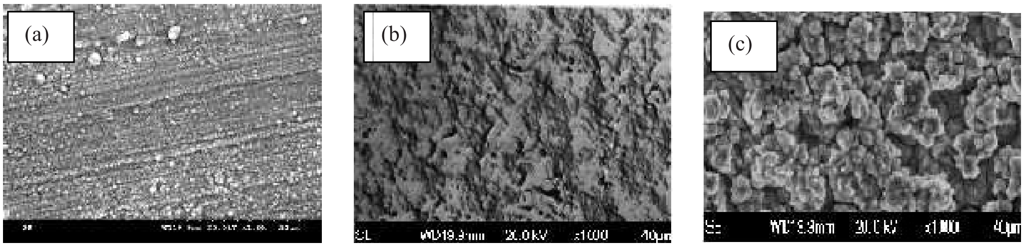


Fig. 2. SEM images of (a) Trivalent black chromium; (b) Coatings after annealing at 300°C; (c) Coatings after annealing at 400°C.

## 3.4 Corrosion resistant measurements

### 3.4.1 Potentiodynamic polarization studies

The results of potentiodynamic polarization studies obtained for the corrosion of mild steel coated with trivalent chromium both in the as plated as well as annealed conditions are presented in figure 3.

This study indicated that the black coatings effectively reduced the corrosion of mild steel in 3.5%NaCl. The $E_{corr}$ value for mild steel is -894 mV which is shifted to positive direction for the black coatings both in the as plated as well as annealed conditions. The black coatings annealed at 300°C, display better corrosion resistance than the coatings annealed at 400 °C. This can be ascribed to the formation of precipitation of intermetallic compounds as well as the consistent distribution of trivalent chromium coatings on mild steel. These results are in good agreement with XRD and SEM analysis.

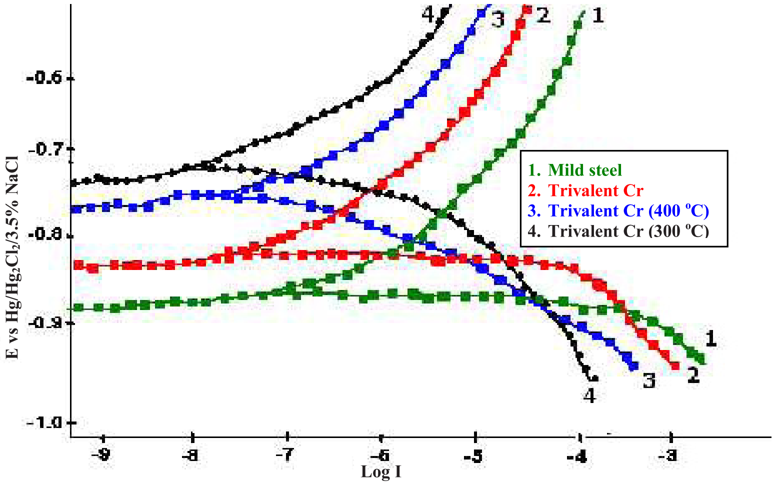


Fig. 3. Potentiodynamic polarization curves for the corrosion resistance of trivalent Cr coatings in seawater.

### 3.4.2 Electrochemical Impedance Spectroscopy (EIS) measurements

The impedance data for the corrosion of carbon steel substrate and black coatings in 3.5% NaCl solution are shown in figure 4. It is evident that the formation of a single semicircle is a characteristic of metallic coatings [15-16]. Although the circles in the Nyquist plot seems to be similar based on their shape, they differ significantly in their sizes. The semicircle at the high frequency region stands for the coating response, while the sphere at the low frequency region is associated with simultaneous physicochemical phenomena at the metal/coating/solution interface .The sphere at the lower frequency region is related with the diffusion of the oxides through the black coating [17-18]. The introduction of constant phase equivalent [CPE] into equivalent circuit has not significantly altered the charger transfer resistance values. This might be due to the homogeneity in coatings formation on the steel surface. The calculation of CPE, from τ (relaxation time) and n (surface uniformity) were made using the relations, $Z_{CPE} = \frac{1}{c_{dl}\left[\left(-1/\tau\right)_n\right]^{-1}}$ of Warburg-Nyquist plots [19].

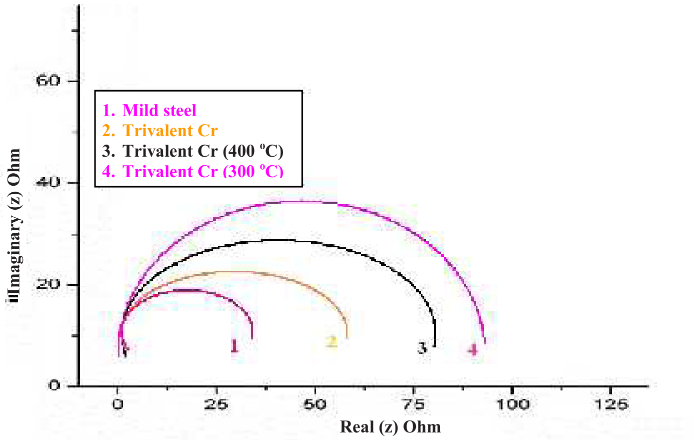


Fig. 4. Nyquist plots for the corrosion resistance of trivalent Cr coatings in seawater.

Table 3. Impedance values of trivalent black chrome coatings
Medium: 3.5% NaCl

| System | $R_t$ (Ohm. cm$^2$) | $C_{dl}$ (µF.cm$^{-2}$) | CPE (µF.cm$^{-2}$) | Surface uniformity, n | Relaxation time, τ (x $10^{-5}$) | Corrosion resistance (%) |
|---|---|---|---|---|---|---|
| Mild Steel | 35 | 29 | 35 | - | - | - |
| As plated Cr | 59 | 17 | 59 | 0.413 | 11.6 | 41.3 |
| Annealed Cr at 400 °C | 78 | 6.4 | 78 | 0.77 | 5.7 | 77.9 |
| Annealed Cr at 300 °C | 93 | 1.17 | 93 | 0.95 | 1.25 | 95.9 |

The black coated steel has the highest values of $R_t$ and lowest values of $C_{dl}$ implying the better anti-corrosion ability (Table 3). The $R_t$ values of steel, trivalent chrome coatings both as plated and after annealing at 300 °C and 400 °C are 35,59, 93 and 78 ohm and the corresponding $C_{dl}$ values are 29, 17, 1.17, 6.4 µF.cm$^{-2}$. The higher values of charge transfer resistance of the coatings after heat treatment might be due to the formation of intermetallic phases of Co-P and Cr-Co. The relaxation time (τ) and surface uniformity (n) for coated samples indicated that coatings annealed at 300 °C, exhibited better corrosion resistance than the others. As the relaxation time for coatings decreases, the rate of corrosion reaction diminishes. It indicates that the time required to attack the mild steel surface by $Cl^-$ is delayed by the trivalent chromium coatings. The enhanced values of n for the annealed coatings obtained at 300 °C established that the said coating is highly resistant to attack of $Cl^-$ in neutral media due to the enlarged surface uniformity.

### *3.5 Evaluation of absorption of light*

Table 4. Optical properties of the films obtained in the trivalent Cr plating

| Deposition time (min.) | Absorption (α) | Emittance (ε) |
|---|---|---|
| 1 | 0.92 | 0.07 |
| 5 | 0.93 | 0.08 |
| 7 | 0.94 | 0.09 |
| 10 | 0.81 | 0.04 |

Absorption and emission values for the black $Cr^{3+}$ coatings obtained in this study are presented in table 4. It can be visualized from the table that the black nickel coatings have high absorption values. As the coating timing increases, the absorption values change from 0.94 to 0.81 whereas the emittance of the coating increases from 0.09 to 0.04. These results are in good correlation with those reported earlier for black coatings [20-22]. The better absorption and emittance for coatings obtained at 7th minutes is due to highly regular shape, improved micro hardness and less dendrite structure of chromium layers on metal surface. Also, the incorporation of cobalt into the lattice plane of chromate film may enhance optical properties of the coatings. In addition, the current density (0.4 A.cm$^{-2}$) played significant role on the optical properties of the coatings [23]. Hence, these coatings may be used for solar energy applications.

## 4. Conclusion

A suitable bath based on trivalent black chromium coatings with high absorption and emission coefficients have been optimized for corrosion resistance and solar applications. The annealed coatings offered higher hardness due to the precipitation of intermetallic phases as evidenced from X-ray diffraction measurements. SEM investigations showed the uniform dispersion of chromium and cobalt particles in the coatings. The potentiodynamic polarization and impedance parameters justified that the coatings exhibited better corrosion resistance in 3.5% NaCl than mild steel.

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