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Corrosion and abrasion resistance characteristics of trivalent black chromium electrodeposition

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Abstract

An attempt has been made in this work to develop coatings with improved corrosion and abrasion resistance properties based on trivalent chromium which is eco-friendly in nature were tried besides their optical properties. Taber abrasion measurements confirmed the improvement of wear resistance of trivalent black coated surfaces. X-ray photoelectron spectra (XPS) was used to understand the surface morphologies of coatings being responsible for improvement in mechanical properties of automobile components. The enhancement of corrosion resistance is also validated through salt spray analysis.

Keywords trivalent chromium coatings, corrosion resistance, taber abrasion, xps analysis, salt spray

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Introduction

The conventional black coatings involve hexavalent chromium which is highly toxic and banned by Environmental Protection Agency [EPA]. The alternate black coating is trivalent chromium which has to be meticulously formulated to improve hardness, abrasion resistance and corrosion resistance of the coatings.

The development of corrosion resistant black coatings deserves much attention due to their high rate of deposition and inexpensive chemicals usage in industrial process. In general, the black coatings would exhibit better optical properties than mechanical properties. Hexavalent black chromium which is highly toxic was obtained by electrodeposition [Surviliene et.al. [1]] as well as by chromation conversion coatings [Nikolava et.al. [2]]. According to Aguilar et.al.[3], the external layers of black chromium coatings were mainly composed of Cr_2O_3. Anandhan[4] and his co-investigators found that beyond 400^{0}C, the black chromium coatings were found unstable. A trivalent chromium formulation was proposed by Zeinab Abdel Hamid [5] using hexafluorosilicic acid and the resultant coatings has shown superior optical properties i.e. absorption coefficient of 0.97. The above author has used cobalt metal as additive to improve black colour and the optical properties. Bayati et.al.[6] are viewed that the addition of fluride with hexafluorosilicic acid were suitable materials for black chromium coating having absorption coefficient of 0.96. However, the uses of black chromium coatings on improvement of mechanical properties on metallic objects have not been exposed. This lead to an identification of appropriate black chromium coatings to be used for enhancing the wear resistance and corrosion resistances in order to extend the life time of machinery's.

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The performance of coatings is to be evaluated by taber abrasion resistant test, corrosion resistant measurement by electrochemical methods. The surface morphology of the coatings is the predominant properties of the coating which will be assessed by XPS. The absorption coefficient of the coatings is to be evaluated by UV-Visible spectrometer. Salt spray analysis is to be carried out to follow up the corrosion and get an idea about the performance of black chromium coatings.

Experimental procedure

For XPS and wear studies, mild steel specimens of 99.52% purity of size 2 x 5 x 0.2 cm^3 and 100 x 100 x 4 mm^3 were polished with fine grit paper and degreased with trichloro ethylene. They were rinsed in double distilled water. The composition of the mild steel used in the present study is given below:

Carbon = 0.16%; Manganese = 0.3%; Silicon , Sulphur, Phosphorus = Nil; Aluminium = 0.02% and Iron = 99.52%.

The optimized bath used in the present study had the following compositions.

Cr metal (Trivalent) = 54.45 g/l= 270 g $CrCl_3$

Co metal = 6.75 g/l= 20 g $CoCl_2$

NaH_2PO_4 = 6 g/l

NaF = 21 g/l

pH = 4.6

Current density= 200-450 mA/cm^2

Plating time = 7 min.

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Evaluation of black trivalent Cr coatings through different techniques

Taber abrasion resistance measurement

The abrasion resistances of the black chromium coated specimens of size 100 x 100 x 4 mm^3 were measured as per ASTM D-4060 through Taber abraser both in as plated and annealed conditions. The abrading wheels were allowed to rotate on the coatings at a load of 100 g. Before the start of the experiment, the specimens were accurately weighed. Then, the wheels were allowed to rotate against the deposit for 1000 cycles with the above load. After that the specimens were removed and weighed again. The experiment was repeated for another 1000 cycles on the specimens. The average weight loss was taken as the Taber wear index or Abrasion resistance.

Taber wear index = Average weight loss (in mg) for 1000 cycles

Optical properties of black Cr coatings

Solar absorptance of the black Cr coatings were measured with UV visible spectra in the region of wave length from 200 to 400 nm and IR visible were obtained from 750 to 1000 nm regions and low absorptance in the visible region(>400-700 nm) were measured. The absorptance values of the black coatings layers were calculated using Kirchhoff's law, which is given below.

$$A+R+T = 1$$

where A is absorptance, T is transmittance, and R is reflectance of surface. In the opaque surfaces, their transmittance is zero, it can be expressed as:

$$A+R = 1; \text{ so, } A = 1 - R.$$

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Corrosion resistance measurements

Salt spray analysis for corrosion resistance of black coated samples

As per ASTM B-117, the black Cr coated steel panels were tested in SF 850 salt spray cabinet in 3.5% NaCl (sea water medium) to evaluate the corrosion resistance of the coatings. Based on the appearance of formation of red rust spots on the coated samples used under annealed conditions, the corrosion degree of the samples was evaluated.

Surface Characterization (XPS or ESCA analysis)

The black Cr coated samples of size 10 x 10 mm^2 under annealed conditions were used to carry out the surface characterization using a physical electronics PHI 5600 ESCA system (Precision = ±0.2 eV; Vacuum pressure = 10^{-9} Torr) with Al K_{α} monochromatic source was used to obtain oxidation states of species along with chemical composition of surfaces.

Results and Discussions

Taber abrasion resistance

The results of abrasion resistance of the coatings measured by Taber abraser as per ASTM D-4060 are presented in Table 1.

It has been found that the trivalent black chromium coatings improved the abrasion resistance both as plated as well as annealed conditions. This is due to the presence of intermetallic phases by Cr-Co contents. The increased values of abrasion resistance after annealing at 300°C may be due to the precipitation hardening of chromium particles. The results are in good agreement with those reported earlier for electroless deposition of Ni-P-Chromium oxide composite coatings.

Measurement of optical properties

Absorption and emission values for the black Cr^{3+} coatings obtained in this study are presented in Figures 1 and 2. It can be visualized from the figure that the absorption values change from 0.92 to 0.81. These results are in good correlation with those reported earlier for black Cr coatings [7-9]. The better absorption and emittance for coatings obtained at 7th minute 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 the 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 [10]. It was observed from Figure 2 that there is no appreciable change in absorptance for black chromium coatings after annealing at 300°C. Hence, these coatings may be used for solar energy applications.

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Corrosion resistance studies

XPS analysis of Cr black coatings

Figure 3 shows the XPS analysis of the annealed surface of electrodeposited trivalent chromium black coatings clearly showed the presence of the both chromium and cobalt peaks. The spectrum of the ejected photoelectron displays peaks at the kinetic energy from which binding energy could be inferred. Since the core binding energies are signatures of the elements present, the photoelectron spectra could be used to establish elemental identities.

In the case of chromium, the 2p region showed a doublet $2p_{3/2}$–2p. The peaks for black chromium correspond to the Cr $2p_{3/2}$ core levels. The measured binding energy for $Cr2p_{3/2}$ is very close to binding energies of $Cr(OH)_3$ which as the binding energy of 577.3 eV corresponding to Cr(III). The feeble peak at binding energy value 62.8 eV also showed the presence of Cr^{3+} state. The core peak for cobalt appeared at $Co2p_{3/2}$ with binding energy values 785 eV. The O1s XPS spectrum of the black coatings indicates one chemical states of oxygen at a binding energy of 531 eV.

The bonding in the coatings was composed of F1s and P2p at binding energy values of 313 eV and 295 eV respectively indicating that chromium is attached with oxygen as $Cr(OH)_3$ which occupied the top layer of black coatings.

The trace appearances of flurine atom and phosphorus atomic peaks have come from the additives. i.e. sodium fluride and sodium dihydrogen phosphate. The binding energy value of O KLL at 1008 eV which is in close proximity to $Co2p_{3/2}$ peaks at binding energy 785 eV confirming that cobalt is existing as Co_3O_4 in the inner layer of the coatings evidence from their higher binding energy values compared with $Cr(OH)_3$.[11-12]

Analysis of salt spray test

The results of salt spray test are shown in table 2. The progress of corrosion on black coated steel samples using trivalent chromium coatings as well as the uncoated steel is shown.

For steel samples, it was noticed that 30% red rust formed on uncoated sample at 30 minutes stay in salt spray chamber. 2% rust area formation on trivalent black chrome after 960 hours stay in salt spray chamber.

Therefore, it can be concluded that corrosion resistance of black trivalent chromium coatings in salt spray is 32 times higher than uncoated steel specimens.

Conclusions

1. A suitable eco-friendly bath has been formulated based on trivalent chromium, cobalt and sodium dihydrogen phosphate.
2. Trivalent black coated surfaces enhanced the abrasion resistance both in the as plated as well as annealed condition.
3. The precipitation hardening of Cr particles resulted intermetallic phase formation by Cr-Co contents.
4. The existence of $Cr3+$ in the coatings was evidenced from binding energy values by XPS analysis.
5. The trivalent chrome coated surfaces could with stand up to 960 hours salt spray resistance which is 32 times higher than mild steel.

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Table 1 Abrasion resistance for trivalent black chromium coatings

S.No.	Nature of the system	Taber wear index (load 1000g) for 1000 cycles (in grams)	
		As plated	Annealed at 300°C
1.	Trivalent chromium coatings	0.024	0.018

Table 2 Results of salt spray analysis as per ASTM B-117

Time (hr)	Uncoated Steel	Appearance of black Trivalent Cr coatings
0	White	Black
0.5	30% red rust area	Black
1	100% red rust area	Black
36	100% red rust area	Black
120	100% red rust area	Black
240	100% red rust area	Black
480	100% red rust area	Black
960	100% red rust area	2% red rust
1100	100% red rust area	5% red rust
1200	100% red rust area	30% red rust area

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Legends for figure

1. Absorption results for trivalent black chromium coatings (as plated)

2. Absorption results for trivalent black chromium coatings (annealed)

3. XPS analysis of trivalent black chromium coatings

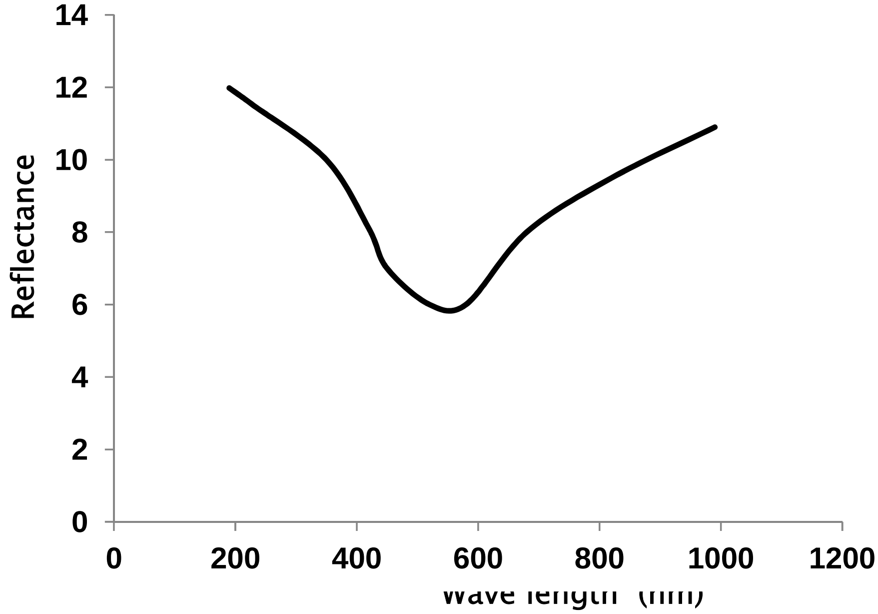

Figure 1

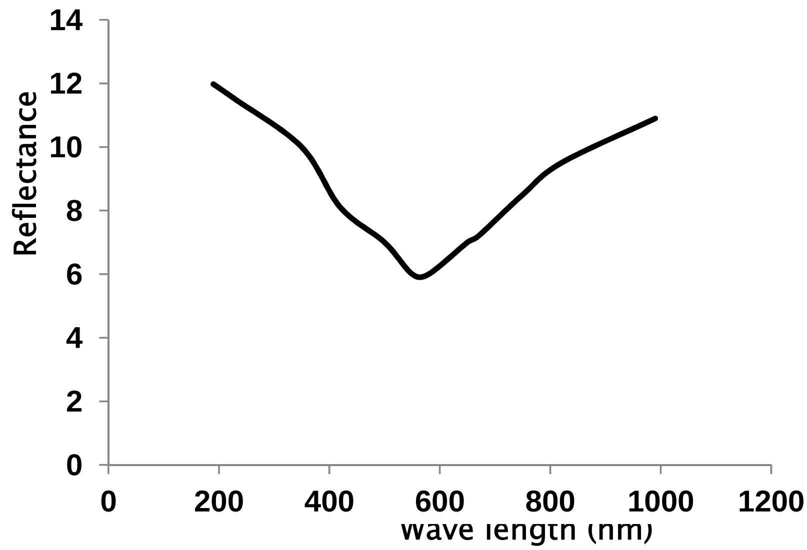

Figure 2

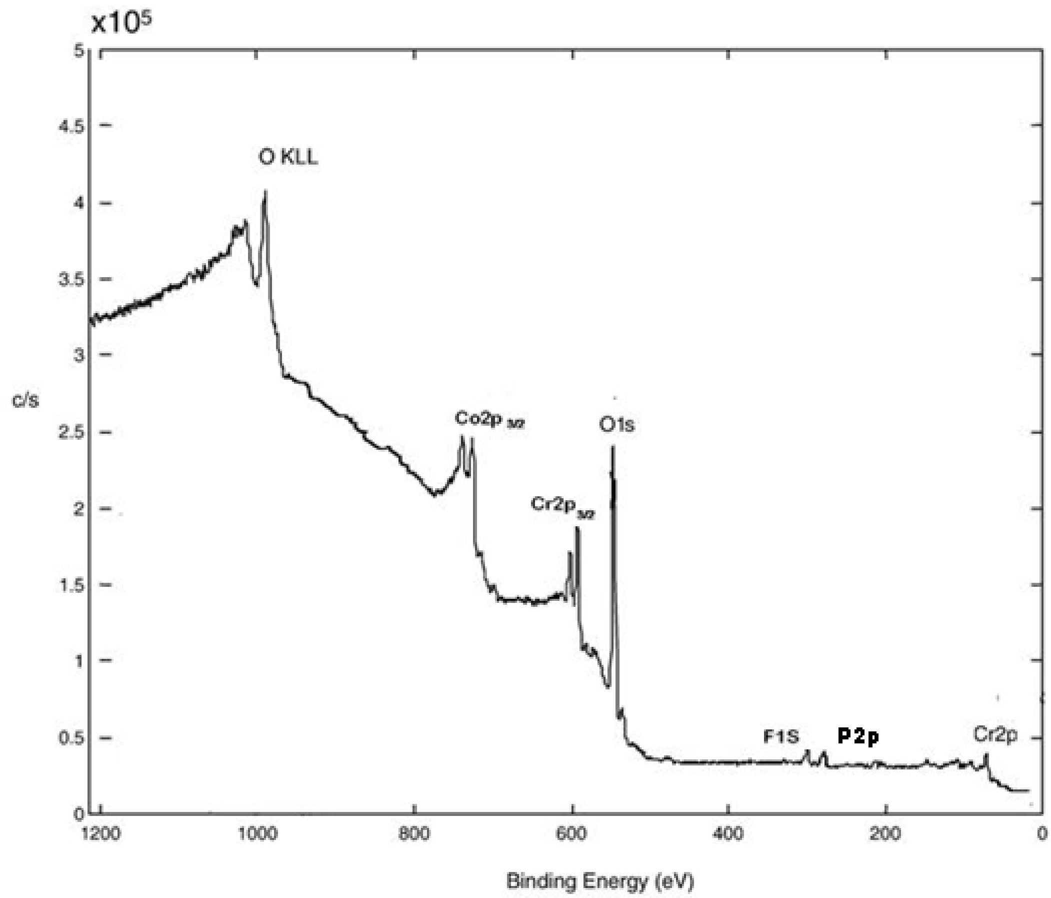
x10⁵
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
c/s
O KLL
Co2p 3/2
O1s
Cr2p 3/2
F1S
P2p
Cr2p
1200
1000
800
600
400
200
0
Binding Energy (eV)

Figure 3