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XPS analysis of corrosion resistant black trivalent chromium and ternary black Ni-Cu-Co electrodeposited automobile components

P.A. Jeeva[1], S. Karthikeyan[2*], S. Narayanan[1]
School of Mechanical & Building Sciences, VIT University, Vellore – 632 014, India
[*]Surface Engineering Research Lab., Centre for Nanobiotechnology, VIT University, Vellore – 632 014, India

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[*]Corresponding author. E mail: skarthikeyanphd@yahoo.co.in ; Tel : (+91 78453 00117)

Abstract
An attempt has been made to analyze the surface analysis of the black coatings using a trivalent chromium coating and nickel based ternary coating. X-ray photoelectron spectroscopy (XPS) analysis confirmed that the existence of chromates, oxides, nickel, cobalt and copper in the black coatings. From the appearance of the species at the surface, binding energy and electron level were reported. The improvement of corrosion resistance was observed with black Ni-Cu-Co using salt spray analysis.

Keywords: Black coatings, Trivalent, Ternary, XPS analysis, Salt spray analysis.

Introduction
Black coatings used for both decorative and solar absorbing functions are mostly prepared by liquid phase deposition or vapour phase deposition [1-3]. Black nickel and black chromium are the important category of materials produced by electrodeposition. The nickel based black coatings have been widely used in solar collectors and gas turbines. Despite of its excellent optical properties the applications of black coatings on improvement of mechanical properties on metallic objects have not been explored [4-7]. This lead to an identification of appropriate black coatings to be used for enhancing the mechanical properties in order to enable to extend life time of machineries [8]. 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. In order to improve the rate of deposition with simultaneous significant contribution to mechanical properties of automotive components, ternary alloy coatings will be developed based on Ni-Cu-Co with high deposition rate. The surface morphology of the coatings is the predominant properties of the coating which will be assessed by XPS analysis.

2. Materials and methods
2.1. Apparatus
For trial studies, mild steel specimens of 99.52% purity of size 10 x 10 mm^2 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 was given below:
Carbon = 0.16%;
Manganese = 0.3%;
Silicon, Sulphur, Phosphorus = Nil;
Aluminium = 0.02% and
Iron = 99.52%

2.2 Optimized Bath composition of trivalent chrome and Ni-Cu-Co
2.2.1 Black Trivalent chrome coatings
$CrCl_3$ = 270 g/l
$CoCl_2$ = 20 g/l
NaH_2PO_4 = 6 g/l
NaF = 21 g/l

pH = 4.6
Current density= 200-450 mA/cm^2
Plating time = 7 min.

2.2.2 Black Ni-Cu-Co coatings
$NiSO_4.6H_2O$ = 40 g/l
$CuSO_4.6H_2O$ = 8 g/l
$CoSO_4.5H_2O$ = 15 g/l
Ammonium thiocyanate = 25 g/l
Boric acid = 30 g/l
EDTA = 3 g/l
pH = 4.7
Current density = 400 mA/cm^2
Plating time = 180 seconds

Figure 1: Radiator drain plug

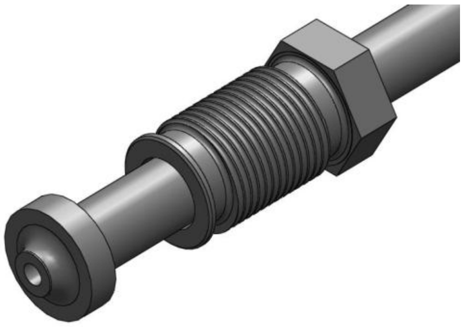

Figure 2: Vehicle brake tube

The above bath formulations have been used to develop black coatings on radiator drain plug (Figure 1) and vehicle brake tubing system (Figure 2) used in automotive industries. For measurement of mechanical properties and evaluation of surface properties mild steel specimens were used as discussed above.
The surface characterization measurements were carried out on black coated samples under annealed conditions using X-ray photoelectron spectra in a physical electronics PHI 5600 ESCA system with Al K_α monochromatic source was used to obtain oxidation states of species along with chemical composition of surfaces. The binding energy values were calculated with a precision of ±0.2 eV. For these measurements, the samples were mounted in to an ultra high vacuum chamber at 10^{-9} Torr housing the analyzer. Prior to mounting, the black coated samples were placed in the preparation chamber for 6 hours in order to remove any volatile species exist on the surface.
For salt spray analysis, the black coated radiator drain plug and vehicle brake tubes of thickness 35 microns for each system were used. The analysis was carried our as per ASTM B 117 procedure.

3. Results and discussion

3.1 XPS analysis of trivalent chromium black coatings

The XPS analysis of the electrodeposited trivalent black chromium coatings after annealing at 300°C clearly showed the presence of the both chromium and cobalt peaks. 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 [9]. 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 $Cr(OH)_3$ [10-13].

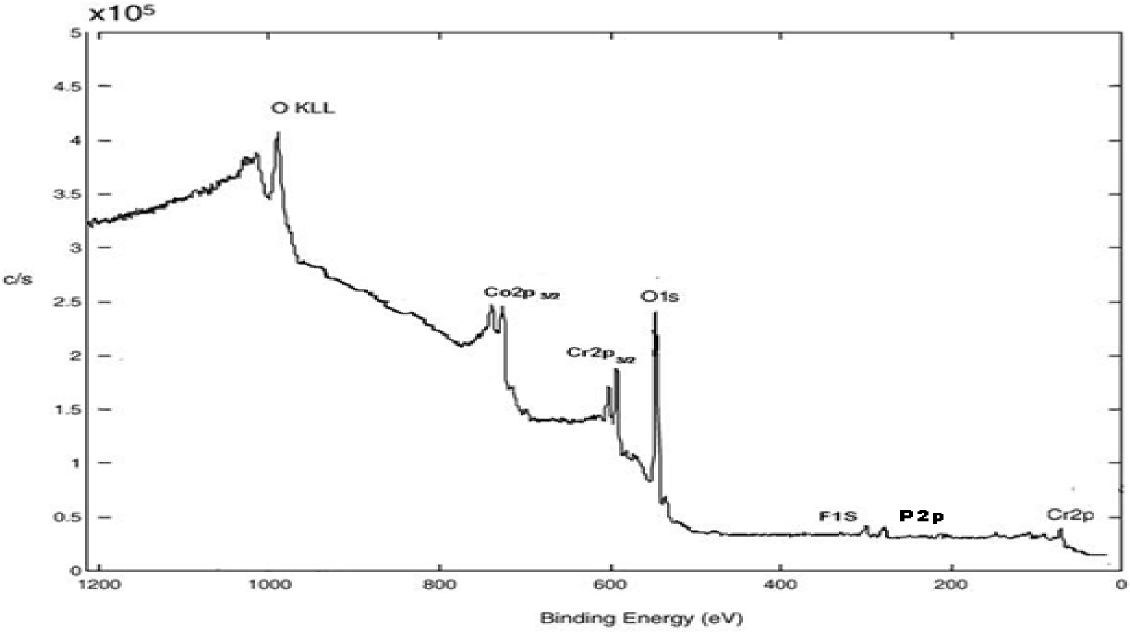

Figure 3: XPS analysis of trivalent black chromium coatings

3.2 XPS analysis of Ni-Cu-Co black coatings

The annealed ternary Ni-Cu-Co black coatings were subjected to XPS analysis in order to determine the oxidation state of particular elements in the deposits. The core peak of cobalt appeared as $Co2p_{3/2}$ at binding energy 785 eV along with appearance of Cu3p peak at binding energy of 45 eV confirming that copper and cobalt are existing as their oxides with oxidation state of +2.

This is further confirmed by the formation of O1s peak with binding energy value 531 eV. The traces of C1s, S1s and N1s at binding energy values 213 eV, 162 eV and 127 eV have shown the utility of ammonium thiocyanate which acted as a complexing agent for nickel ions to prevent powdery deposits. The formation of sulphur binding energy values resembled a report as described earlier [14-15].

The appearance of core peaks i.e. doublet peaks for nickel as Ni $2p_{3/2}$ and Ni 2p along with a singlet strong peak of Cu $2p_{3/2}$ and O KLL at their corresponding binding energy values of 853 eV, 839 eV, 933 eV and 1008 eV establishing that at inner layers nickel is existing as NiO with oxidation state of +2. Similar is the trend with copper which existed as CuO with oxidation state Cu(II).

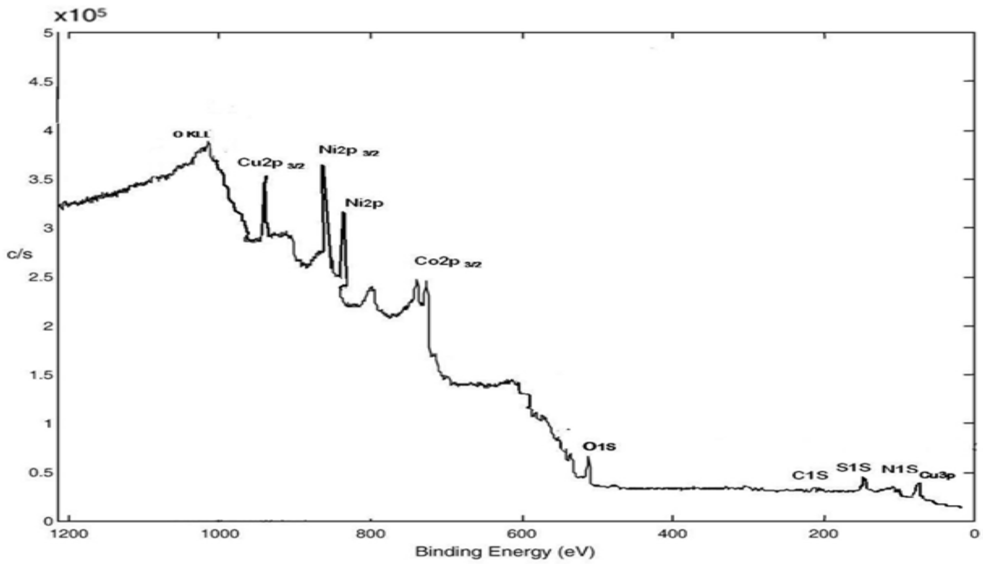

Figure 4: XPS analysis of Ni-Cu-Co black coatings

The following table summarizes the results XPS studies obtained for black coatings.

Table 1: Results of XPS studies obtained for black coatings

S.No.	Coatings	Species identified	Binding energy (eV)	Electron level	Appearance at the surface
1.	Trivalent Black Cr	$Cr(OH)_3$ as Cr^{3+}	577.3	Cr $2p_{3/2}$	Outer layer
		Co_3O_4	785	Co $2p_{3/2}$	Inner layer
		O	1008	O KLL	Inner layer
2	Black Ni-Cu-Co	Co^{2+} as CoO	785	Co $2p_{3/2}$	Outer layer
		Cu^{2+} as CuO	45, 933	Cu 3p, Cu $2p_{3/2}$	Inner and outer layers
		O	531, 1008	O 1s, O KLL	Outer layer Inner layer
		Ni^{2+} as NiO	853, 839	Ni $2p_{3/2,}$ Ni 2p	
		C,S,N	213, 162, 127	C 1s, S 1s, N 1s	Outer layer

3.3 Analysis of Salt Spray Test

The results of salt spray test for Ni-Cu-Co black coatings are presented in table 2. The progress of corrosion on black coated steel samples using trivalent chromium has been reported elsewhere [16].

For steel samples, it is noticed that 30% red rust formed on uncoated sample at 30 minutes stay in salt spray chamber.

Therefore, it could be justified that corrosion resistance of black Ni-Cu-Co coatings in salt spray is 40 times higher than the uncoated steel coupons. As reported earlier [16], the corrosion resistance of trivalent black chromium was 32 times higher than uncoated steel.

Based on the above studies, the following order of performances of black coatings can be concluded as Ni-Cu-Co > Trivalent Cr.

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

Time (hr)	**Uncoated Steel**	**Appearance of black coatings**
		Ni-Cu-Co
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	Black
1100	100% red rust area	Black
1200	100% red rust area	2% red rust area

Conclusion

1. The formulations of suitable plating bath have been arrived by trial and error methods and the optimized plating baths have been reported.
2. XPS analysis has clearly demonstrated the oxidation states and nature of individual atomic species exist in the black coatings evidenced from the binding energy values.
3. The corrosion resistance performance of black coatings in salt spray test followed the order as given below.
   Ni-Cu-Co > Trivalent Cr.

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