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Studies On The Electrodeposition Of High Speed Black Coatings

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Abstract: An attempt has been made in this work to develop black coatings using a high speed electroplating baths based on Nickel, Copper, Cobalt, Complexing and buffer agents. The black coatings obtained enhanced the absorbtion of sunlight (UV-Visible) .The surface morphology of coatings have been assessed by XRD and SEM studies. The corrosion resistances of the coatings in sea water were evaluated by A.C. impedance analysis.
Key words: Electrodeposition Of High Speed Black Coatings.

1.Introduction

A black object is prepared from a material that absorbs all inward light (all the colours of the visible spectrum). In reality, objects which look black reflect always some light and as a result the ideal black object does not exist. There is no material on earth that absorbs 100% of light at all angles and over all wavelengths.

In the field of surface treatments, black coatings are extensively used for decorative or solar absorbing functions. The films deposited should have high optical properties (absorption of solar radiations). Black coatings used for both decorative and solar absorbing functions are mostly prepared by liquid phase deposition or vapour phase deposition. Black nickel and black chromium are the most significant electrodeposited materials, whereas the films elaborated by vapour phase deposition comprise generally titanium alloys and carbon based materials. The studies on black coatings based in electrodeposition of nickel alloys in recent years are gaining much value as they discover a great range of applications in different fields like solar absorbance and gas turbines.

2 Literature survey on black coatings obtained by electrodeposition

Black nickel [1-3], black zinc[4], black chromium [5], black phosphate[6] and black molybdenum [7, 8] based alloys are the most known black coatings obtained by liquid phase deposition. Among all, nickel based alloys and chromium based alloys have been particularly studied and are widely used for their efficient conversion of solar radiation into thermal energy.

Nickel and nickel based alloys

The black nickel coatings may be prepared by electroless [9] or electroplating techniques onto various metal substrates [10-13]. Chemical conversion of a zinc-coated substrate is another way to obtain black nickel coatings [14-17].

Black nickel coatings have been prepared by chemical conversion of zinc-coated aluminum in surface morphology of the base metal on the optical properties of the final coatings. It was reported that the black nickel film prepared on a zinc-coated electropolished aluminum showed absorbance value of the order of 0.90 to 0.94 and emittance ranging from 0.08 to 0.15.

Electrodeposited black nickel may be prepared using sulfate, chloride or sulfate and chloride based baths [18-19]. The black colour is due to the formation of ZnS and NiS particle in the films [20]. Unfortunately, the obtained coatings do not present enough resistance to high humidity at elevated temperatures. To overcome this problem, more stable black coatings have been electrodeposited in nickel and sodium chlorine aqueous solution [21-23].

A solar absorption and a thermal emittance of 0.96 and 0.10 respectively were reported by the authors and confirmed in another study [24]. In the latter work the author used the bath composition and operating conditions shown in Table 2 to depose a nickel black coating on aluminum and copper substrates. Using quite similar experimental conditions than in the above work [24], black nickel has been electrodeposited on stainless steel substrate [25]. The solar absorption and thermal emittance values obtained were 0.91 and 0.1 respectively.

Mechanical properties and corrosion resistance of black nickel coatings are greatly enhanced when phosphorus is co-deposited with nickel. Electroless black Ni-P with a phosphorus content ranged between 1% and 15% by weight may be obtained by using the composition and operation parameters of plating has been reported by Guofeng Cui et al., [9]. The black treatment was accomplished by etching electroless plating nickel in oxidizing acid solution as follows:

The samples were immersed into 5.5 M sulfuric acid and 4.1 M sodium nitrate solution at 50°C after 10 s. After rinsing and drying, they were introduced into etching solution again for 5 s. [26].

Chemical composition and AFM morphology analysis of the pre-etched and post-etched electroless nickel at various phosphorus content showed that surface became smoother and the nodular structure of the pre-etched film evolved into small convex closure-like structure after black treatment. In addition, etching leads to increase phosphorus content in the film due to a favored dissolution of nickel atoms. Visible reflectance measurements on the films showed that optimum phosphorus content range to prepare low reflectance black nickel from 3 to 7 wt %. In this case, the average reflectance measured at 633 nm was 0.46 ± 0.02.The present investigation is related to the development of black coatings replacing conventional thiocyanate baths.

3. Experimental procedure

Black nickel coatings have been deposited on mild steel by electroplating method. Before deposition, the desired metal plates in dimensions of 2×5 cm^2 were perfectly polished and then thoroughly washed with distilled water. After that, all substrates were degreased with a hot commercial alkaline solution followed by rinsing in distilled water. Finally, they are placed in the chloride electrolyte solution for black nickel plating. Entire coating process is carried out in hull cell. The quality of black nickel coatings depends on the electrolyte solution composition and its concentration, electrodes, solution pH, bath temperature, current density and (deposition) duration (time). Therefore, to obtain optimum optical properties for black nickel coatings, deposition parameters have to be optimized. In this type of coating, the soluble nickel metal is used as a anode with 99% purity. A direct current, 0.5 A/dm^2 was passed between two electrodes in a conducting solution of nickel salts. The chemical bath for black nickel deposition consisted of a mixture of distilled water, nickel, copper, cobalt , boric acid and EDTA by flowing the current through the electrolyte, one of the electrodes (anode) is insoluble made of Ti-Fe alloys, the other electrode (cathode) is covered by a black nickel layer. In the electrolyte solution Ni positive ions (Ni^{++}), Cu^{++} and Co^{++} are present, so as the electrical current flows through the electrolyte, positive ions by absorbing two electrons on the surface of cathode are converted to nickel, copper and cobalt metals and deposited on the cathode surface. Reverse reaction occurs at the anode. The concentrations of metals were varied to improve the optical performance. After numerous tests, the best conditions for strongly adherent and durable black nickel coating, as mentioned in **Table 1**, were obtained as follows: solution with pH 4.2, electrolyte bath temperature 37°C, plating time 8 min and current density 0.5 A/dm^2. The optical, corrosion resistant and structural properties of the black nickel coatings have been investigated. SEM and XRD analysis were carried out by Philips PW3710 and Philips XL 30; the absorption spectra of coatings were performed by Jasco UV-VIS respectively.

Table 1. The composition of baths used for obtaining black coatings

S.No	Bath Composition	Operating conditions	Observations
1.	$NiSO_4$ - 20 g/l $CuSO_4$ - 4 g/l $CoSO_4$ - 7 g/l Boric acid - 30 g/l EDTA - 3 g/l	0.5 A/dm^2 8 min. Temp= RT	Uniform black coating.
2.	$NiSO_4$ - 40 g/l $CuSO_4$ - 2 g/l $CoSO_4$ - 15 g/l Boric acid - 30 g/l EDTA - 3 g/l	0.5 A/dm^2 12 min. Temp= RT	Semi-black coating.
3.	**$NiSO_4$ - 40 g/l** **$CuSO_4$ - 8 g/l** **$CoSO_4$ - 15 g/l** **Boric acid - 30 g/l** **EDTA - 3 g/l**	0.5 A/dm^2 **min.** Temp= RT	**Very uniform black coating.**

4. Results and Discussion

Weight gain studies

The results of black coatings obtained in the present study by weight gain method are presented in Table 2.

Rate of deposition (micron/minute) = { Weight gain (in grams) x 10^{-4}/ Density of (Ni+Cu+Co) } x

Area x time (in minutes)

Hardness measurements

The hardness of the electrodeposited Ni-Cu-Co coatings measured by Vicker's hardness tester is given in Table 3.

The higher hardness of black coatings can be ascribed to the formation of uniform metallic layers in the coatings.

Table 2: The results of weight gain studies obtained for black coatings:

S.No	Black coatings	Thickness	Nature of deposit
1.	Sample 1(10 min)	25 microns	Semi black due to peel off nickel layers.
2.	Sample 1(6 min)	24 microns	Semi black with unevenness.
3.	**Sample 1(8min)**	**42 microns**	**Full black with uniformity.**

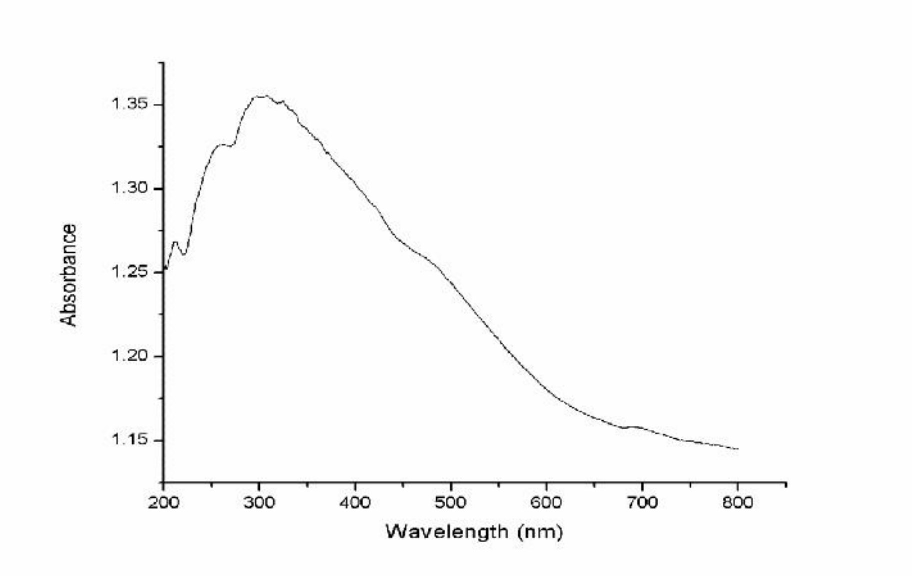
Table 3 Vickers hardness values for black coatings:

Substrate	Hardness in V.H.N (load 100g)
Mild steel	347
Black coatings (42 microns)	**362**

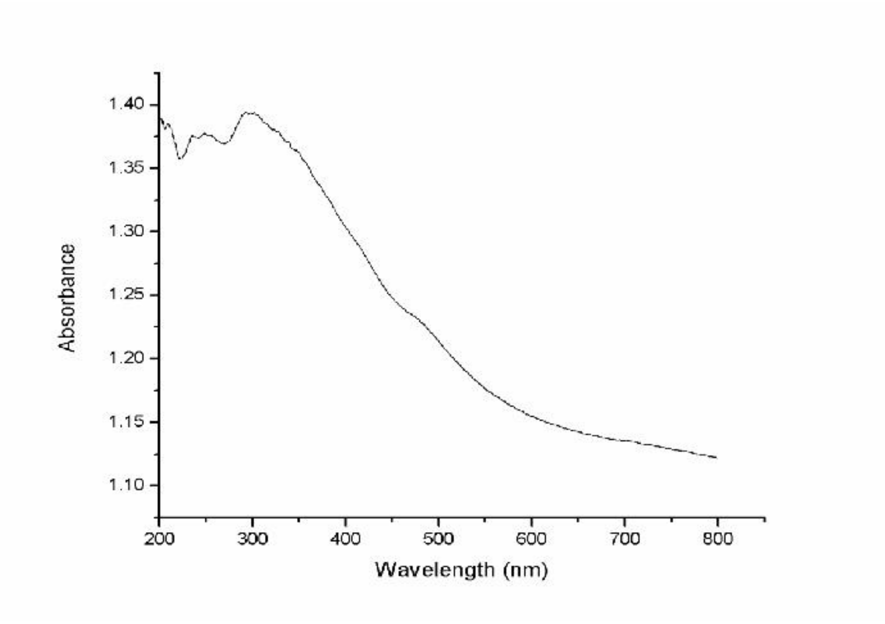
Evaluation of absorption of light

Absorption spectrum curves of the black nickel coatings obtained for various current densities are presented in Fig.1-a , 1-b and Fig.1-c. As can be seen from the graphs below, the black nickel coating has high absorption coefficient. The results from graphs show that by changing the current density, the absorption spectrum will change. The best absorption is related to the coating layer for sample 3 (fig.1c) at 1.32 ,followed by sample 1(fig.1.a) at 1.35 and sample 2 (fig 1b) at 1.39.

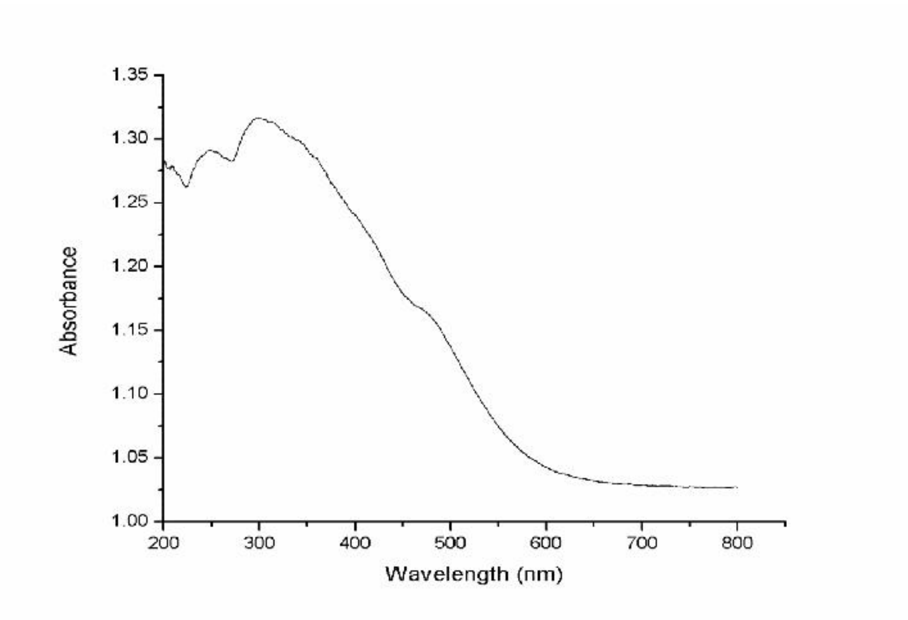
Absorbance graphs-UV VISBLE SPECTRA



Sample 1 –Figure 1.a



Sample 2-–Figure 1.b



Sample 3-––Figure 1.c (Optimized bath)

Corrosion resistance studies- Electrochemical Impedance Spectroscopy (EIS) studies

The measured impedance spectra of the carbon steel substrate and black coatings in 3.5% NaCl solution are shown as Nyquist plots in Fig.2. It is evident from Fig. -2 that the formation of a single semicircle or a semicircle in the high frequency region followed by a low frequency loop is typical of metallic coatings [25,26]. Although the curves in the Nyquist plot appear to be similar with respect to their shape, they differ considerably in their sizes. The semicircle at the high frequency region represents the coating response, while the loop at the low frequency region is associated with simultaneous physicochemical phenomena at the metal/coating/solution interface .The loop at the lower frequency region is associated with the double layer capacitance and/or diffusion phenomena of the oxidant chemical species through the porous coating in the case of mild steel[27-32].

The R_t and C_{dl} values increased and decreased, respectively, for the black coatings. The black coated steel has the highest values of R_t and lowest values of C_{dl} implying the better anti-corrosion ability. The R_t of black coated steel is 2740 and the corresponding C_{dl} value is 1.48 µF cm^{-2}.The R_t and C_{dl} values for mild steel are 1767 and 3.26µF cm^{-2}.

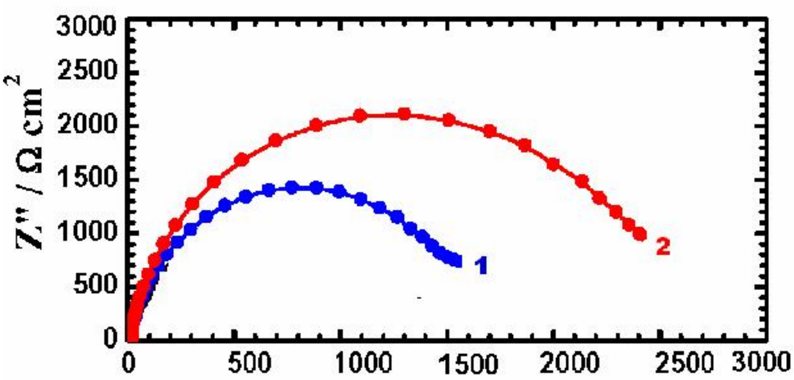


Figure 2 .Nyquist plots for 1.mild steel 2. Black coatings ; medium – 3.5% NaCl

Surface morphology of the electroless copper coatings

X-ray diffraction analysis

The results of XRD analysis are shown **in** Fig. 3. The crystalline peaks are resulted from the nickel and alloys. A broad dominant peak appearing around d value of 1.98 indicates the existence of nickel in the black coatings. The feeble peaks at d values of 2.3 and 1.41 correspond to the presence of copper and cobalt metals in the black coatings which accounts for the highest hardness of black coatings than mild steel substrate. A thin peak at d value 7.66 corresponds to the formation of Nickel oxide in the black coatings. This result is in good agreement with result of EDAX analysis.

Scanning Electron Microscopic studies

Fig. 4 shows the cross sectional morphologies of black coatings obtained from nickel electroplating bath.

It can be found that the morphology changes remarkably. For the black coatings, the best evenness and compactness can be observed and needle holes hardly appear on its surface, as evidenced from SEM images.

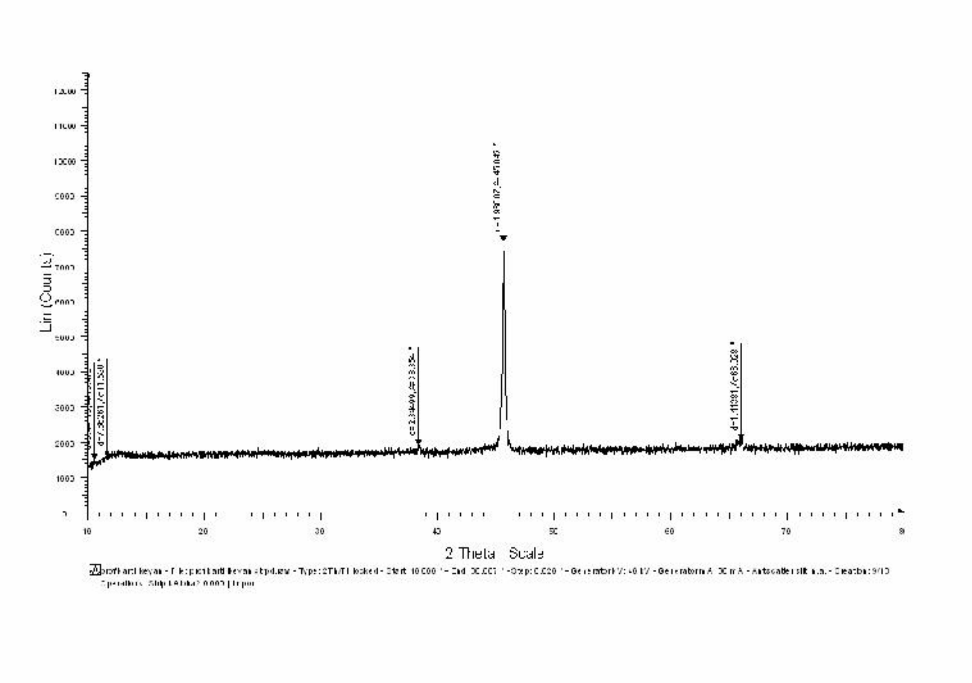


Figure 3.XRD results for black coatings

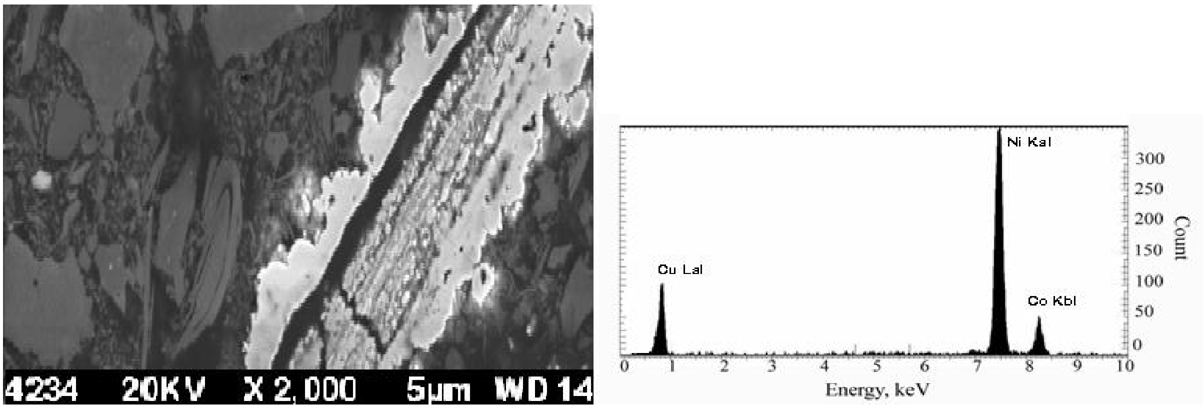


Figure 4.Cross sectional SEM image for black coatings

6.Conclusion:

The black nickel coatings with high absorption coefficient are suitable for solar applications. The coatings are very adhesive and high absorption coefficient. SEM images show the uniform dispersion fine nickel, cobalt and copper particles. X-ray diffraction analyses show that black films have crystalline structure and black nickel films were mainly consisting of metallic nickel. This result is matched with result of EDAX analysis. The impedance measurements have proved that the coatings exhibits better corrosion resistance in 3.5% NaCl than mild steel.

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