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INFLUENCE OF p-HYDROXY BENZALDEHYDE ON THE CORROSION PROPERTIES OF Ni–W COATING ON MILD STEEL

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The influence of p-hydroxy benzaldehyde on Ni–W alloy coatings electrodeposited using direct current electroformation in a citrate bath was investigated at different concentrations of additive (0–500 ppm). A stepwise examination of corrosion resistance, crystalline size and microstructure of Ni–W alloy electrodeposits was performed with and without additive in the plating bath. This paper employs Tafel polarization technique and electrochemical impedance spectroscopy (EIS) for corrosion analysis. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used for microstructural analysis. Crystalline size analysis was carried out by means of X-ray diffraction (XRD) method. The results of the investigation showed that the electrodeposition of Ni–W alloy coatings in conjunction with the p-hydroxy benzaldehyde at particular concentration (50 ppm) resulted in improved corrosion resistance (1.4 mm/year), lower surface roughness (57.2 nm) and finer grain size. A Fourier-transform infrared spectroscopy (FTIR) and photoluminescence (PL) analysis ascribed the inclusion and adsorption of additive during electrodeposition process. The optimal additive concentration for the electrodeposition of highly corrosive resistant Ni–W alloy coatings in the studied medium (electrolyte) is 50 ppm.

Keywords: electrodeposition, Ni–W alloy coatings, p-hydroxy benzaldehyde, corrosion measurements, mild steel.

Introduction

Hard chromium is the best known electrodeposit for engineering/functional applications. It is widely used in aerospace, agriculture, fastener, metal manufacturing and oil service industries. Despite their excellent functional properties there is an increasing drive to find a replacement for hard chrome due to environmental concerns of using hexavalent chromium containing sulfate or fluoride as catalysts during the plating process. Conventionally adopted chromium baths (Cr–VI) are becoming obsolete due to the increasing health and environmental awareness and more of alternatives are in practice.

Ni–W is nominated as a promising environment-friendly alloy for replacing hard chromium due to its excellent characteristics, such as stability, high hardness, high wear resistance at elevated temperatures, high melting point, low coefficient of thermal expansion, high tensile strength and high corrosion resistance in many aggressive environment [1,2]. Furthermore, the toxicity towards the aquatic species is low, and the industrial production of these coatings will produce environmentally harmless wastewater [3]. Moreover, its robust corrosion resistance property, i.e. corrosion rate of Ni–W film in HCl solution at 30^0C was only 1/40 of 304 stainless steel [4] that anticipates its use in as the barrier between copper and silicon in the next generation of ultra large scale integration circuits (ULSI) and micro electromechanical systems (MEMS) [5].

Electrodeposition is a technologically feasible and inexpensive method to fabricate strong and relatively ductile metallic materials in bulk form or as coatings [6]. It has gained a significant importance as an attractive surface-finishing technique for wear and corrosion protection, enabling coating on substrates of complex geometrical forms and large surfaces with high uniformity of thickness (from nanometres up to several tens of micrometres [2]. It has several advantages, of low capital investment, easy handling, good reproducibility, controllable electrochemical parameters, and reduction of waste [7]. Further, its usage has become increasingly crucial for engineering advancements [8]. Usage of additives

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in the electrolytic baths is highly encouraged due to their addition in small amounts (ppm), that helps in the formation of smooth and shiny deposits and the effluent treatment is easier [9–11]. The usage of 4-hydroxy-benzaldehyde in Zn–Mn alloy baths, significantly improved their surface morphology and increase in Mn percent in the coatings and consequently found to be as a levelling agent [12,13].

The present study deals with the effect of p-hydroxy benzaldehyde on the Ni–W alloy deposits derived from citrate bath as reported [14]. Efforts were taken to investigate the influence of p-hydroxy benzaldehyde at different concentrations in the bath, on the corrosion resistance properties of Ni–W alloy deposits and further the surface morphology and phase structure of the deposits were studied in comparison with that of as such deposits.

Experimental

Electrodeposition aspects

Bath solution was prepared using AR grade chemicals dissolved in double distilled water. The detailed electrolyte composition and operating conditions are given in Table 1. The pH of the bath was adjusted to 8.0 adding H_2SO_4 solutions. Mild steel plates of dimensions of (25 mm×25 mm×0.3 mm) were employed as cathodic substrates. Desired surface of the specimens was cleaned with acetone, mechanically polished with diamond paste using twin disc polisher. Further they were subjected to electro-cleaning in alkaline solution [15]. Prior to the deposition, desired surface was activated in H_2SO_4 solution for 10 seconds to remove the oxide film from the surface and instantly placed in the plating bath. After alloy deposition the specimens were flushed with water in order to remove the rudimental solutions from the surface of the coatings and then blow-dried. Platinised titanium of dimensions (25 mm×25 mm×1.5 mm) was used as anode. Electrodeposition of alloy coatings was done in a usual thermostated glass cell at a constant tempera-ture of 333±3 K. The temperature was maintained constantly with thermostat during deposition. Experiments were done in triplicate to optimize the additive concentration and stability of additive in the bath.

Table 1

Basic bath composition and processing conditions

Bath constituent	Content (M)	Working conditions
$NiSO_4{\cdot}6H_2O$	0.1	Temperature 333±3 K
$Na_3WO_4{\cdot}2H_2O$	0.2	Current density 5 A/dm^2
$C_6H_5Na_3O_7{\cdot}2H_2O$	0.5	pH 8
NaCl	0.1	Deposition time 15 min
NH_4Cl	0.5	Anode – platinized
$C_7H_6O_2$	0–500 ppm	titanium

Characterization of electrodeposits

The obtained electrodeposits were subjected to various characterization techniques to study their physical and corrosion properties. The corrosion behaviour of alloy coatings in 0.2 M H_2SO_4 solution was analysed by means of Tafel polarization and electrochemical impedance spectroscopy (EIS) studies. A standard three electrode electrochemical cell was used, wherein Ni–W alloy deposits with an exposed area of 0.2 cm^2 was used as working electrode, saturated calomel electrode and platinum wire as reference and counter electrodes respectively. After attaining the steady state open circuit potential (OCP), polarization curves were recorded, with a potential window of ±200 mV from OCP at sweep rate of 10 mV/s. Impedance measurement were done at OCP with the voltage perturbation amplitude of 5 mV in the frequency range from 1Hz to 100 KHz. The obtained plots were fitted using commercial available software Z-view of version 3.0. Electro-chemical measurements were done with the help of computer-controlled potentiostat/galvanostat CHI660C at ambient temperatures.

The phase structure of the obtained deposits was investigated using X-ray diffraction spectrometer, Shimadzu XRD 6000 using Cu–K_α radiation. The crystallite size of the deposits, were calculated using the Scherrer equation:

$$d=(0.9\lambda)/(\beta\cos\theta), \quad (1)$$

where d is the average crystallite size, λ is the wavelength of X-ray, β is the full-width at half-maximum (FWHM), and θ is the scattering angle.

The morphology and composition of alloy were investigated using, scanning electron microscopy couple energy dispersive spectroscopy (SEM–EDX) analyser (JSM-360; JEOL). The inclusion of additive in the deposits was attained with the help of Fourier transform infrared spectroscopy (FTIR) (IR Prestige-21 Shimadzu, Japan). Photoluminescence measurements were performed using a JASCO Model FP-8200 system with a xenon flash lamp and gratings to provide the required excitation, to examine the adsorption of additive on the alloy surface.

Results and discussion

Electrodeposition

Electrodeposition of Ni–W alloys containing citrate as complexing agent proceeds through the following reactions [16]:

$$[(Ni)(Cit)]^- + [(WO_4)(Cit)(H)]^{4-} \rightarrow \rightarrow [(Ni)(WO_4)(Cit)(H)]^{2-} + Cit^{3-}; \quad (2)$$

$$[(Ni)(WO_4)(Cit)(H)]^{2-}+8\bar{e}+3H_2O\rightarrow$$
$$\rightarrow NiW+7OH^-+Cit^{3-}. \quad (3)$$

Corrosion studies

Fig. 1 depicts the Tafel curves of Ni–W alloy deposits in 0.2 M H_2SO_4 solution, deposited from the citrate bath containing different concentrations of p-hydroxy benzaldehyde (0–500 ppm). The following Tafel parameters, including corrosion current (i_{corr}), corrosion potential (E_{corr}), linear polarisation resistance (R_p), calculated corrosion rate (CR), and protection efficiency (PE) are listed in Table 2.

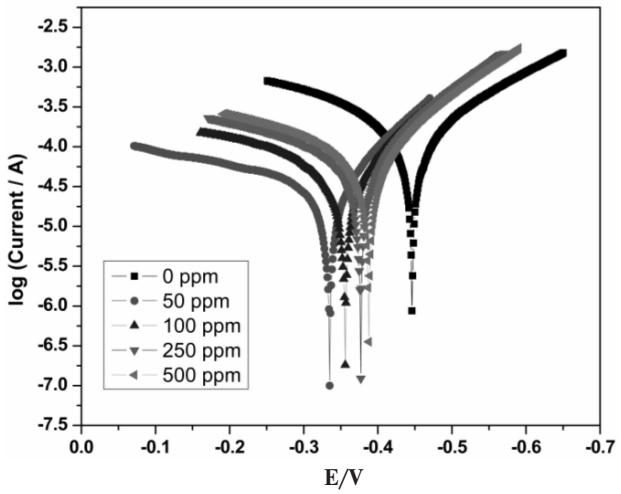

Fig. 1. Typical Tafel plots of Ni–W alloy coatings in 0.2 M H_2SO_4 medium. The electrodeposits were obtained in absence and in presence of different concentrations of p-hydroxy benzaldehyde in the bath solution

It is noteworthy that a high positive value of E_{corr} and low value of i_{corr} are obtained for the alloy deposits, deposited from the bath containing 50 ppm of p-hydroxy benzaldehyde; while the blank one showed low positive value of E_{corr} and high value of i_{corr}. These changes in the value of E_{corr} and i_{corr} indicate that the p-hydroxy benzaldehyde coated sample (50 ppm) possess good corrosion resistance towards the simulated physical environment. However, as the concentration of addition agent increases in the bath, the coatings resulted in the low positive value of E_{corr} and high value of i_{corr} that eventually resulted in the high corrosion rate. The corrosion rate also decreased for the deposits obtained from the bath containing 50 ppm of protocatechuic aldehyde, with that of blank one. This decrease in the corrosion rate infers that added aldehyde helped in blocking the active corrosion sites, and helped in the formation of protective film on the surface of alloy through adsorption. High polarization resistance value of 1125.1 Ω cm^2 is obtained for the aldehyde coated sample (50 ppm) in 0.2 M H_2SO_4 solution; while the blank one resulted in low value of polarization resistance i.e. 254.9 Ω cm^2. This change in the R_p values infers that the aldehyde coated sample (50 ppm) had higher protection efficiency than that of blank one (Table 2). PE from the corrosion current values was calculated using the following equation:

$$PE(\%) = \frac{i^0_{corr} - i^i_{corr}}{i^0_{corr}} \times 100 , \quad (4)$$

where i^0_{corr} and i^i_{corr} are the corrosion current densities of Ni–W alloy coatings obtained from the bath without and with additive, respectively.

Electrochemical impedance spectroscopy (EIS) is one of the powerful and non-destructive techniques which help in studying the corrosion behavior of specimen at the electrode/electrolyte interface in the simulated physical environment. The values generated from the equivalent circuit are shown in Table 3. The Nyquist plots were shown in Fig. 2. Charge transfer resistance (R_{ct}) is calculated from the diameter of semicircles. Increase in the R_{ct} and decrease in the C_{dl} is noticed for the alloy deposits obtained upon addition of 50 ppm of additive in the bath. However, at higher concentrations, decrease in the R_{ct} and increase in the C_{dl} is observed. Among all, the deposits obtained from the bath containing

Table 2

Polarization parameters derived from Tafel plots in 0.2 M H_2SO_4 in absence and presence of various concentrations of p-hydroxy benzaldehyde in the bath

Concentration of p-hydroxy benzaldehyde (ppm)	E_{corr} (mV vs. SCE)	i_{corr} (μA/cm^2)	CR (mm/year)	R_p (Ω cm^2)	PE (%)
0	–0.446	166.9	6.87	254.9	–
50	–0.335	33.68	1.4	1125.1	77.34
100	–0.356	47.07	2.0	790.8	67.76
250	–0.377	65.67	2.8	561.2	54.57
500	–0.388	75.91	3.2	491.7	48.15

50 ppm of p-hydroxy benzaldehyde resulted in high R_{ct} (1064.2 Ω cm²) and low C_{dl} (38.04 μF/cm²) values. This results advocates that the added additive has been adsorbed on the cathode surface which resulted in a compact deposit. Thus low C_{dl} value is obtained which infers that contact of active area with the corrosive environment is decreased. The possible locale for the adsorption of p-hydroxy benzaldehyde, is the free electrons present on the oxygen atom of carbonyl group. P-hydroxy benzaldehyde consist of hydroxyl group (strong electron donating group) which helps in donating electrons to the carbonyl group, thus how helps in increasing electron density or cloud. Either through one of the forces or all, i.e. adsorption, electrophoresis or convection, the adsorption of additive takes place within the matrix during electrodeposition and helps in the formation of compact structured electrodeposits [17]. This finally resulted in a high corrosion resistant Ni–W alloy coating. However, at higher concentrations, the decrease in the R_{ct} and increase in the C_{dl} values may be due to the partial coverage of the electrode surface by the additive, which in turn blocks the active sites and decreases the nucleation rate, and affects the nucleation mechanism, caused by aldehyde decomposition during electrodeposition [18].

PE given in Table 3 was calculated from the charge transfer resistance by the following equation:

$$PE(\%) = \frac{R_{ct}^{i} - R_{ct}^{0}}{R_{ct}^{i}} \times 100 , \qquad (5)$$

where R_{ct}^{i} and R_{ct}^{0} denote the charge-transfer resistance of Ni–W alloy coatings with and without p-hydroxy benzaldehyde, respectively.

Based on the discussion and results obtained from the electrochemical parameters, it was concluded that the alloy coatings obtained from the bath containing 50 ppm of p-hydroxy benzaldehyde, showed a high corrosion resistance towards corrosive medium.

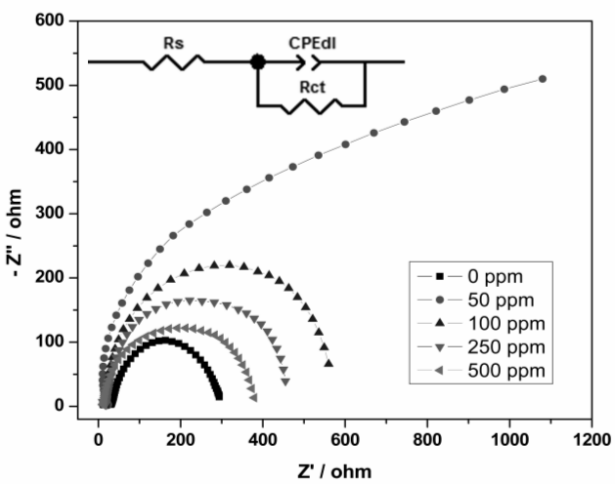

Fig. 2. Nyquist plots of Ni–W alloy coatings in 0.2 M H_2SO_4 medium. The electrodeposits were obtained in absence and in presence of different concentrations of p-hydroxy benzaldehyde in the bath solution. Proposed equivalent circuit model contains: R_s – solution resistance, R_{ct} – charge transfer resistance, and CPE_{dl} – double layer capacitance

XRD study

Fig. 3 depicts the X-ray diffraction spectra of Ni–W alloy obtained in the absence and presence of additive in the bath. The XRD patterns show that Ni–W alloy was found to crystalline in faced centered cubic (JCPDS data cards of # 87-0712, # 88-2339). The average crystalline size, of the deposits obtained in the presence of additive is reduced significantly (10.0 nm) against blank (12.0 nm). The characteristic peaks of Ni (111) and W (222) are remarkable. The decrease in the peak intensity and peak broadening was observed in case of aldehyde coated deposits against the blank. These changes infer that the presence of additive in the bath helps in decreasing the crystalline size [19] by enhancing the electrocrystallization of metals during electrodeposition.

Table 3

Charge transfer resistance values of Ni–W electrodeposits in 0.2 M H_2SO_4 in absence and presence of various concentrations of p-hydroxy benzaldehyde

Concentration of p-hydroxy benzaldehyde (ppm)	R_s (Ω cm²)	C_{dl} (μF/cm²)	n	R_{ct} (Ω cm²)	PE (%)
0	29.92	44.76	0.81	269	–
50	15.85	38.04	0.91	1064.2	74.72
100	15.15	39.46	0.89	546.2	50.75
250	16.93	47.38	0.86	444.7	39.50
500	9.45	48.46	0.82	367.4	26.78

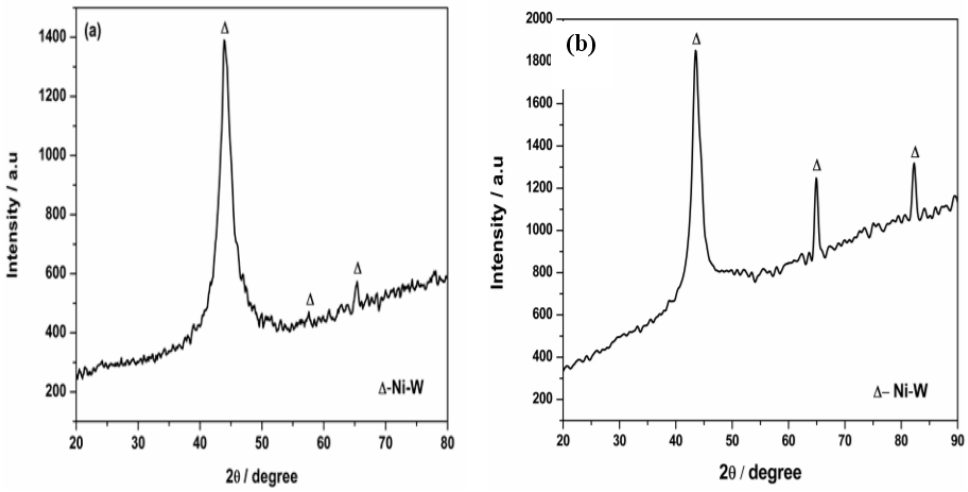

Fig. 3. X-ray diffraction patterns of Ni–W alloy electrodeposits, deposited from the bath (a) without additive (b) with additive (50 ppm)

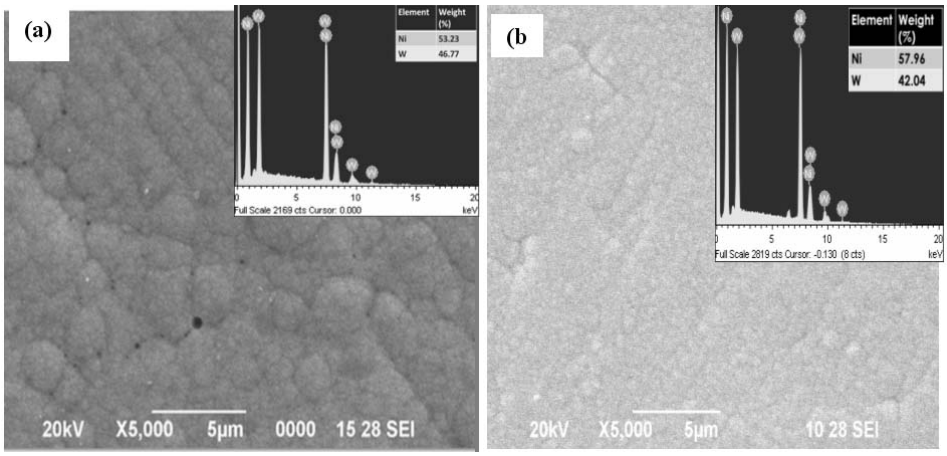

Fig. 4. SEM-EDAX photomicrographs of Ni–W alloy deposits (a) in the absence (b) in the presence of p-hydroxy benzaldehyde (50 ppm) in the plating bath

SEM-EDAX study

The obtained electrodeposits from the bath containing p-hydroxy benzaldehyde (50 ppm) were uniform, smooth and bright with that of blank. Figure 4 depicts the SEM-EDAX micrographs of Ni–W alloy deposits obtained from the baths, in the absence and presence of additive (50 ppm). The morphology of the blank shows the deposit with non-uniform, coarse grained texture, and porous in nature. The deposits obtained from the bath containing additive (50 ppm) are relatively smooth and uniform. The addition agent helped in the formation of fresh nucleation sites and retards the crystal growth. Moreover, it acts as pore filler, filling the micron holes of the deposits. Thus how, the delayed crystal growth resulted in the fine grained deposits. The weight percentage of elements present in the deposits was evaluated with the help of EDAX technique.

The coating composition of Ni–W alloy deposits of as such and deposit obtained from the bath containing p-hydroxy benzaldehyde (50 ppm) are also shown in Fig. 4. The weight percentage of elements obtained in the absence of additive is Ni – 53.23% and W – 46.77%, while the element weight percentage of deposits obtained in the presence of additive is Ni – 57.96% and W – 42.04%, respectively.

AFM study

Surface topography of Ni–W electrodeposits, obtained in the absence and presence of additive (50 ppm) in the bath; was carried out using atomic force microscopy. 2D and 3D pictures of AFM are shown in Figs. 5 and 6. The advantage of AFM is its capacity to probe minute details to the individual

grains and intergrain regions [20]. Surface roughness of Ni–W alloy deposits was reduced in the case of deposits obtained in the presence of additive (50 ppm) in the bath (57.2 nm), compared to those alloy deposits (72.5 nm) obtained in the absence of additive in the bath. Fig. 5 shows that deposit consists of grains with larger aggregates on the entire surface. This leads to the roughness of deposits. While, the Fig. 6 displays fine aggregates with apparent hills and valleys, which may be caused by structural transition [21]. The smaller surface roughness may be conditioned by progressive nucleation during electrodeposition.

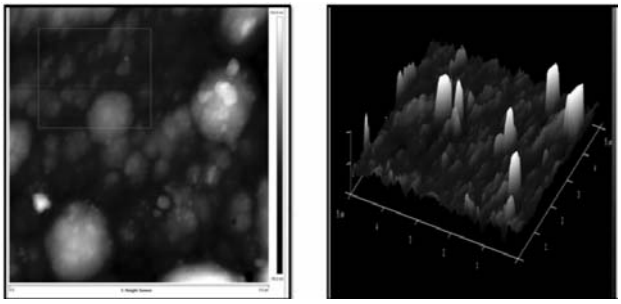

Fig. 5. 2D and 3D AFM images of Ni–W alloy electrodeposits electrodeposited in the absence of additive

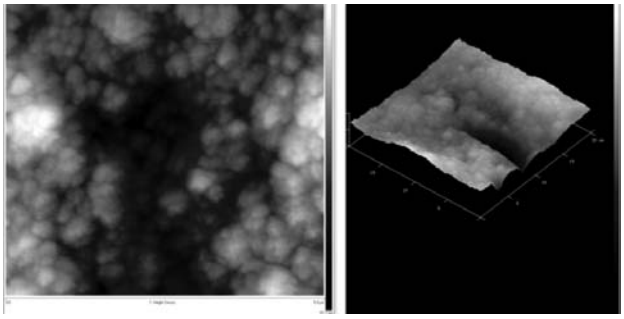

Fig. 6. 2D and 3D AFM images of Ni–W alloy electrodeposits obtained from the bath containing p-hydroxy benzaldehyde (50 ppm)

FTIR spectra

The IR spectrum of Ni–W alloy deposit, obtained in the presence of addition agent (50 ppm) was shown in Fig. 7. The spectrum shows absorption peak around 680.0 cm^{-1} is assigned to the aromatic –C–H stretching. The absorption peak at 1630.0 cm^{-1} is assigned to the C=O stretching and the peak at 2250.0 cm^{-1} is assigned to the C≡C stretching of aromatic ring and the peak at 3434.40 cm^{-1} corresponds to –OH (hydroxyl) group of addition agent. Thus the obtained spectra revealed the incorporation of additive within the matrix of the deposits during electrodeposition.

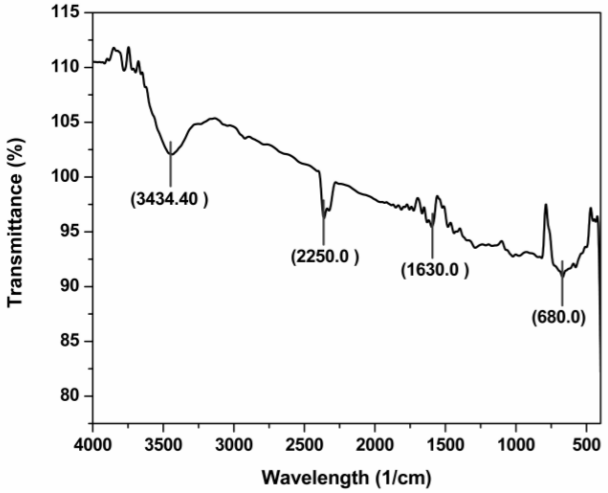

Fig. 7. FTIR spectra of Ni–W alloy electrodeposits deposited from the optimized bath (50 ppm)

Photoluminescence spectra

To further verify the adsorption of the additive molecule on the alloy surface, photoluminescence spectra was recorded. Fig. 8 shows the photoluminescence (PL) spectra of Ni–W alloy coated samples without and with p-hydroxy benzaldehyde (50 ppm) for the excitation wavelength (λ_{ex})=246.0 nm. Enhancement in the PL intensity is noticed for the deposits (Fig. 8(b)) obtained from the bath containing additive (50 ppm) against blank Fig. 8(a)). The increase in the PL intensity implies that the metal has been coordinated with the carbonyl group of p-hydroxy benzaldehyde molecule i.e. chelation enhanced fluorescence (CHEF). We believe that this study provides a piece of evidence for the adsorption of additive molecules on the alloy surface.

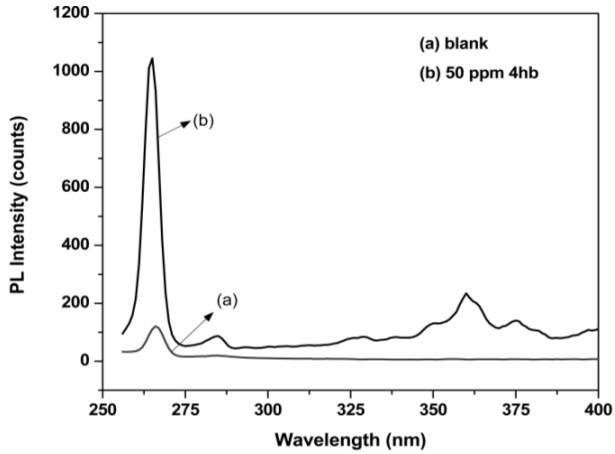

Fig. 8. PL spectra of Ni–W alloy deposits obtained from the bath (a) without (b) with additive (50 ppm)

Conclusions

Ni–W alloy coatings were deposited by applying direct current onto mild steel substrates from alkaline citrate electrolytes containing different concentration of p-hydroxy benzaldehyde (0–500 ppm). Morphology and composition of the alloys were analyzed by SEM and EDAX studies respectively. XRD was used to determine crystalline size of electrodeposit. Corrosion properties of the coatings were investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a sulphuric acid medium. It was found that alloys deposited in presence of additive (50 ppm) in the bath, resulted in low corrosion rate of 1.4 mm/year and high charge transfer resistance of 1064.2 Ω cm^2 contributing to the satisfactory corrosion results of Ni–W alloy coatings under the conditions studied. Nanocrystalline, uniform and fine grained deposits were obtained from the optimized bath revealed by XRD result. Inclusion and adsorption of additive in the electrodeposits was proved using FTIR and PL spectroscopy analysis, respectively.

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Keywords: electrodeposition; Ni–W alloy coatings; p-hydroxy benzaldehyde; corrosion measurements; mild steel.

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