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Effect of salicylaldehyde on microstructure and corrosion resistance of electrodeposited nanocrystalline Ni–W alloy coatings

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ABSTRACT

In this paper, nanocrystalline Ni–W alloy coatings were deposited from citrate bath containing salicylaldehyde (0–500 ppm). The structure, microstructure and surface roughness of coatings were separately analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscopy (AFM). The corrosion resistance of the Ni–W alloy coated specimens was evaluated using potentiodynamic polarization (Tafel) and electrochemical impedance spectroscopy (EIS) studies. Results indicated that electrodeposits obtained in the presence of additive (100 ppm) in the bath were, nanocrystalline, uniform and smooth in their texture. A low value (7.02 μA/cm^2) of corrosion current and high value (1666.90 Ω cm^2) of charge transfer resistance supports for its superior corrosion resistance property. The inclusion of additive in the deposit was evidenced by FT-IR spectra.

1. Introduction

Acidic solutions are widely used in the industries due to the applicability in the chemical cleaning of scale in metallurgy, oil recovery, petrochemical industry and in the acid pickling of iron and steel [1]. During this acidic application, in particular with the use of hydrochloric and sulphuric acid the corrosion of metal is extreme [2]. Moreover, the sulphate ion is more aggressive than the chloride ion in neutral and alkaline medium solutions provoking pitting [3]. The protection of metals from corrosion is always a hot topic to be dealt with, which aids in increasing the lifetime of metal and reducing the economic loss per year. Ni–W alloy coatings offer a promising feature of superior corrosion resistance property along with good mechanical and tribological properties. S. Yao et al. found out that Ni–W is more corrosion resistant than the stainless steel 304 in acidic medium among the considered alloys [4]. It was proved that Ni–W (28 wt.%) is the most stable alloy in the sulphuric acid medium [5]. As this alloy preparation process is in accordance with the consideration of environmental protection, it can therefore become a good substitute for hard chromium [6]. Moreover its satisfactory appearance, good mechanical and anti-corrosion properties makes this alloy as the most promising alternate alloy to replace hard chromium [7]. Consequently, Ni–W alloy coatings have raised a lot of interests in acting as barrier layers for ultra large scale and micro-electromechanical system applications and as an alternative for use in micro-mould injectors, computers and polymeric components [8–9]. Electrodeposition has proven to be an adaptable technique to fabricate metallic nanostructures, especially alloy thin films just by varying electrochemical parameters like current density, temperature, time, and pH [10]. Further, this process can yield porosity-free deposits that do not require subsequent consolidation processing [11]. The nanocrystalline Ni–W coating exhibits higher hardness and scratch resistance as compared with pure nanocrystalline Ni coating, although the contribution of solid-solution strengthening from W is expected to be essentially negligible [12].

While most studies on the electrodeposited Ni–W coatings have been concentrated on their process parameters, studies of the additives are limited. The effect of aldehydes, substituted aldehydes and a condensation product of aldehydes were studied enormously in the alloy plating baths such as Zn–Ni and Zn–Fe alloys [13–14]. Further, the adsorbed additives can affect the activation energy, rate of charge transfer in the electrochemical reaction and also the mechanism of electrocrystallization during electrodeposition [15]. Few researchers have studied the effect of salicylaldehyde as alone and its condensation product and in combination with different additives in the zinc plating baths [16–18]. However, the literature on the usage of salicylaldehyde as an additive in the Ni–W alloy plating baths is absent. In this paper, the use of salicylaldehyde as an additive for improving corrosion behaviour of Ni–W coating is considered and efforts were also made to investigate the influence of salicylaldehyde on the surface morphology and phase structure of the deposits.

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2. Experimental process

2.1. Electrodeposition of Ni–W coatings

Bath solution was prepared using AR grade chemicals in double distilled water. The detailed electrolyte composition and operating conditions are given in Table 1. To the freshly prepared bath, salicylaldehyde (additive) was added in a concentration of 0, 50, 100, 250 and 500 ppm. The electrolyte composition reported in the literature [19], was used as the base bath in this study. The pH of the bath was adjusted to 8.0 using 5% H_2SO_4 or NaOH solutions. Mild steel (Fe—96.14 wt.%, O—3.86 wt.%) plates with dimensions of 25 mm × 25 mm × 0.3 mm were used as cathode substrates. The desired surface of the specimens was cleaned with acetone, mechanically polished to attain a mirror finish, with a diamond paste using twin disc polisher. Further, they were subjected to electro-cleaning in alkaline solution [20]. Prior to the deposition, the desired surface of steel was activated in 5% H_2SO_4 solution for 10 s and then immediately placed in the plating bath. After alloy deposition, the specimen was flushed with water and left for air drying. Platinized titanium of dimensions (25 mm × 25 mm × 1.5 mm) was used as an anode. Electrodeposition of alloy coatings onto mild steel were done in a usual thermostated glass cell at a constant temperature of 333 ± 3 K. Temperature was maintained constantly during deposition, using an automatic controller. Experiments were done in triplicate to optimize the additive concentration in the bath.

2.2. Characterization of Ni–W coatings

The obtained electrodeposits were subjected to various characterization techniques to study their physical and corrosion properties. The deposit thickness was measured with the help of METRAVI (CTG-01) coating thickness tester, and the corresponding final values were determined as the average of 10 measurements. The corrosion behaviour of Ni–W coatings in 0.2 M H_2SO_4 solution was analyzed by means of Tafel polarization and electrochemical impedance spectroscopy (EIS) studies. A standard three-electrode electrochemical cell was used, wherein Ni–W alloy coated steel, with an exposed area of 0.2 cm^2 was used as working electrode, saturated calomel electrode and platinum foil with a larger area as reference and counter electrodes respectively. After attaining the steady state open circuit potential (OCP), potentiodynamic cathodic and anodic polarization curves were recorded, with a potential window of ± 200 mV from OCP at a sweep rate of 10 mV/s. Impedance measurement was done at OCP with the voltage perturbation amplitude of 5 mV in the frequency range from 1 Hz to 100 kHz. The obtained plots were fitted using commercially available software Z-view (V.3.0). Electrochemical measurements were done with the help of computer-controlled potentiostat/galvanostat CHI660C (USA) at ambient temperatures. To have satisfactory reproducibility, electrochemical measurements were repeated four to five times for each condition.

The PE was calculated from the corrosion current values using the following equation:

$$PE(\%) = \frac{i^0_{corr} - i^i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

Table 1
Bath composition and parameters.

Bath constituents	Concentration (M)	Operating conditions
$NiSO_4 \cdot 6H_2O$	0.1	Temperature: 333 ± 3 K
$Na_2WO_4 \cdot 2H_2O$	0.2	Current density: 5 Adm^{-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 titanium
$C_7H_6O_2$	0–500 ppm	Cathode- mild steel

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

PE was calculated from the charge transfer resistance by the following equation:

$$PE(\%) = \frac{Rct^i - Rct^0}{Rct^i} \times 100 \quad (2)$$

where R^i_{ct} and R^0_{ct} denote the charge-transfer resistance of Ni–W coatings deposited in the presence and absence of with and without salicylaldehyde in the bath, respectively.

The Ni–W deposit which is having high corrosion resistance is subjected to the further studies. Deposit obtained from the bath without aldehyde is also studied for comparison.

The phase structure of the obtained deposits was investigated using XRD spectrometer, Shimadzu XRD 6000 (Japan) instrument equipped with a Cu-Kα radiation source. The crystallite size of the deposits from the obtained XRD results was calculated using the Scherrer equation,

$$d = (0.9\lambda)/(\beta \cos\theta) \quad (3)$$

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

The morphology and composition of the deposited alloys as mentioned in the XRD studies were investigated using scanning electron microscopy couple energy dispersive spectroscopy (SEM-EDS) analyser (JSM-360; JEOL). A high-resolution atomic force microscopy (AFM) (Bruker-Dimension icon AFM equipped with a Scan Asyst) was used to know the surface roughness of the alloy deposits at atomic resolution. 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 the X-ray photoelectron spectroscopy (XPS) measurements were performed with a XPS instrument (Carl Zeiss) equipped with Ultra 55 FESEM with EDS. All the spectra were acquired at a pressure using an ultra-high vacuum with Al-Kα excitation at 250 W.

3. Results and discussion

3.1. Electrodeposition

Electrodeposition of Ni–W coatings, containing citrate as complexing agent proceeds through the following reactions Eqs. (4) and (5). Further, it was found that citrate containing baths resulted in the increase in tungsten content [10].

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

$$[(Ni)(WO_4)(Cit)(H)]^{2-} + 8e^- + 3H_2O \rightarrow NiW + 7OH^- + Cit^{3-} \quad (5)$$

The graph representing the effect of additive concentration on the thickness of the Ni–W coatings was shown in Fig. 1. The average thickness of the deposits varied from 33.5 (blank) to 56 μm (100 ppm). A prominent thickness of 56 μm was obtained for the alloy deposits, deposited from the bath containing salicylaldehyde (100 ppm). However at higher concentrations i.e. above 100 ppm in the bath it resulted in lower thickness. One of the possible reasons for the decrease in the thickness of the deposits is the adsorption of additive on the plating surface; decreasing or hindering the effective area on the electrode free for Ni–W electrodeposition. Furthermore, the obtained electrodeposit from the bath containing salicylaldehyde (100 ppm) was uniform, smooth and bright.