Influence of Positional Isomeric Spacers of Naphthalene Derivatives on Ni–W Alloy Electrodeposition: Electrochemical and Microstructural Properties

Uppalapati Pramod Kumar,* Tongxiang Liang,* C. Joseph Kennady, Raju Nandha Kumar, and Jayaraj Prabhu

ABSTRACT: Herein, Ni–W alloy matrixes were successfully fortified with two salen-type Schiff bases 1-(E)-(2-(E)-(2-hydroxynaphthalen-1-yl)-methyleneamino)phenylimino)methyl)naphthalen-2-ol (OPD) and 1-(E)-(2-(E)-(2-hydroxynaphthalen-1-yl)methyleneamino)phenylimino)methyl)naphthalen-2-ol (PPD) as additives, of similar molecular structure but varied isomeric spacers, using a facile direct current electrodeposition technique. The resulting coatings from the additive-introduced reaction system were termed as Ni–W/OPD and Ni–W/PPD throughout the study. The deterioration process (0.5 M H2SO4), surface properties, elemental composition, functional groups, and structures of the resultant coatings were analyzed by means of Tafel and electrochemical impedance spectroscopy, field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy, atomic force microscopy, energy dispersive X-ray spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction (XRD). The bare Ni–W alloy deposition resulted in a loose microstructure with higher porosity density (12.2%), while that of additive-doped plating electrolytes resulted in a compact and dense microstructure with lesser porosity density (6.3%) and minimal porosity density (3.7%) as for Ni–W/OPD and Ni–W/PPD alloy coatings, respectively. Improved corrosion parameters presented superior corrosion characteristics of Ni–W alloy coatings from an additive (PPD)-induced bath, i.e., Ni–W/PPD. Synergetic adsorption of imine groups (N atoms), hydroxyl groups (O atoms), and aromatic electron clouds and reduction in steric hindrance produced by a larger isomeric spacer strengthened the surface adsorption of additives, yielding a fine nanocrystalline Ni–W coating with reduced porosity and well-refined grains, implying the outstanding shielding effect. Results of FESEM, AFM, and XRD analyses revealed a complete cohesion between two neighboring islands, resulting in a fine planar structure with minimal coating defects for Ni–W/PPD coatings, authenticating the corrosion parameters.

1. INTRODUCTION

Prior to 1937, the utilization of tungsten heavy alloys or heavy metal alloys along with the addition of low-temperature elements (Ni, Co, and Cu) has provided high strength or toughness and ductility.1,2 Over a period of time, the concept of the application of this type of matrix (Ni–W) as a protective coating has gained significant interest with the major thrust coming from the ordinance sector (replacement of depleted uranium as kinetic energy penetrators),3–8 heavy duty electrical contact materials, plasma-facing materials in steric hindrance produced by a larger isomeric spacer strengthened the surface adsorption of additives, yielding a fine nanocrystalline Ni–W coating with reduced porosity and well-refined grains, implying the outstanding shielding effect. Results of FESEM, AFM, and XRD analyses revealed a complete cohesion between two neighboring islands, resulting in a fine planar structure with minimal coating defects for Ni–W/PPD coatings, authenticating the corrosion parameters.

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nanostructure against coarsening. Among the diverse surface modification techniques, such as microarc oxidation, powder metallurgy, physical vapor deposition, chemical vapor deposition, etc., electrodeposition has become a favorable choice owing to its simplicity and affordability and being time saving and economically affordable.\textsuperscript{14,15} This traditional technique is one of the most established techniques and enables to tailor the metallic coatings (composites, alloys) uniformly at high growth rate on an industrial scale.\textsuperscript{16} Moreover, the technique is quite versatile that aids in achieving single/multilayered coatings on complex geometries, which improves the lustrous property\textsuperscript{17} and functional property and extends the service life of machinery parts that can be applied in various engineering fields.\textsuperscript{18,19} To date, the administration of organic additives into alloy electrolytes is in practice, primarily as a best corrosion mitigation tool. However, it plays multiple roles as a brightener, stress reliever, leveling agent, grain refiner, tensile ductility improver, and complexing agent.\textsuperscript{1,17,20,21} These additives are easy to handle, economically pragmatic, and offers pertinent solubility in the metal electrolytes without any agglomeration as that for nanoparticles.\textsuperscript{22} Moreover, the presence of infinitesimal, highly efficient, multiple/conjugated bonds (C=C, C=N, C=O, etc.), inherent π electrons, and heteroatoms (N, O, S, and P) contributes to the effective adsorption contiguity that triggers the corrosion reduction process. Studies on the application of salen-type Schiff bases as corrosion inhibitors have been reported.\textsuperscript{23—25} The application of naphthalene and its derivatives as additives in the plating baths has been reported, subject to its varied role in the action of play. The subjected naphthalene derivatives acted as an internal stress reliever in nickel Watts-type baths;\textsuperscript{26} upon addition of naphthalene-1,3,6-trisulfonic acid to the Pd deep eutectic solvent system, thin, dense, compact, and smooth deposits were formed,\textsuperscript{27} and it also acted as a good hardening agent in Ni–Co binary alloy coatings.\textsuperscript{28} However, less attention have been focused on the application of this type of additives (similar geometry and varied spacer) in a Ni–W ion solution (plating bath). The present work has been carried out with intention to explore the effect of additives (OPD and PPD) on the corrosion-resistant property of Ni–W alloy coatings with the aid of electrochemical measurements. Further, their scientific underpinnings were elaborated using field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and energy dispersive X-ray analysis.

2. EXPERIMENTAL SECTION

2.1. Film Preparation. The molecular structures of employed additives are shown in Figure 1, and their synthesis and characterization are reported elsewhere.\textsuperscript{20} The fabrication of the identified Ni–W alloys was achieved on a copper substrate from the target composition tabulated in Table 1. A platinized titanium sheet (25 mm × 25 mm × 1.5 mm) and a Cu sheet (25 mm × 25 mm × 0.3 mm) were employed as an anode and a cathode, respectively, and the distance between the two electrodes was kept constant at 20 mm. First, copper substrates were grounded sequentially with a sand paper and then polished with a diamond paste to attain a mirror finish. Hard cleansing of substrates with acetone was attained under ultrasonic agitation. Second, the substrates were degreased in a solution containing 3.5 g/L NaOH and 2.5 g/L Na2CO3 for 2 min under a galvanostatic mode. Finally, the substrates were subjected to activation in 10% HCl solution for dozens of seconds and transferred to the bath instantly. Sequential rinsing with distilled water was accomplished onto the Cu substrates. During the electrodeposition process, the temperature, pH, CD, and time were maintained constantly at 65 °C, 8, 5 A/dm\textsuperscript{2}, and 15 min, respectively. Finally, the coated samples were rinsed with deionized water, blown with cold air, and desiccated for further characterization. The resultant coatings obtained from the native plating bath (absence of the additive) and that with additives (OPD and PPD) were termed as Ni–W, Ni–W/OPD, and Ni–W/PPD, respectively, throughout the manuscript for brevity.

2.2. Film Characterization. The Ni–W alloy coatings without and with additives (Ni–W/OPD and Ni–W/PPD) were subjected to analysis for surface roughness, morphology, elemental composition, and phase structure, which are interrelated to their electrochemical behavior toward corrosion resistance. The surface appearance, cross-sectional morphology of coatings, substrate adhesion, and elemental composition of the alloy coatings were investigated using an FEI Inspect MLA650F-Brooke Company, Germany) combined with energy dispersive X-ray spectroscopy. The three-dimensional morphology of electrodeposited coatings and the corresponding roughness parameters were calculated using atomic force microscopy (AFM, VEECO D3100). To evaluate the adsorption of additives on the outer layer of the alloy surface and their elemental electronic state, XPS (Thermo Fisher)
equipped with an Al Kα radiation source is adopted. The presence of organic compounds, i.e., functional groups grafted to the Ni–W alloy matrix, was analyzed by a Nicolet NEXUS 870 FTIR (ATR). Furthermore, the phase structure and the average crystalline size were accomplished using XRD (Parnike Xpert PRO MPD) and the Debye–Scherer equation (eq 1). Cu Kα radiation was employed in a scanning range of 20°–90° at 0.02°/s.

\[ d = \frac{(0.9\lambda)}{(\beta \cos \theta)} \]  

(1)

where \( d \) is the average grain size, \( \lambda \) is the wavelength of X-rays, \( \beta \) is the full width at half-maximum, and \( \theta \) is the scattering angle.

Porosity density (PD) in percentage (%) is given as

\[ PD = \frac{R_p \times 10^{-\Delta E/\delta}}{R_p} \]  

(2)

where \( \Delta E \) is the difference between the corrosion potential of the alloy-coated sample and the substrate, \( a \) is the anodic slope of the substrate, and \( R_p \) and \( R_A \) are the polarization resistances of the substrate and the alloy coatings, respectively. A conventional three-compartment pyrex cell filled with 0.5 M H₂SO₄ solution was utilized to perform electrochemical measurements (Tafel and electrochemical impedance spectroscopy (EIS)) on a CHI-660C electrochemical work station. A signal amplitude perturbation of 5 mV relative to the OCP in the frequency ranging from 1 to 100000 Hz was adopted to carry out electrochemical impedance spectroscopy (EIS) measurements. EIS spectra (Nyquist and Bode plots) for the adopted coatings were approximated using Z-View software, version 3. To ensure the reproducibility of corrosion results, the electrochemical measurements were conducted on three replications.

2.3. Corrosion rate (CR) calculation.

\[ CR = \frac{I_{corr} \times EW \times d}{A} \]  

(3)

where CR is the corrosion rate (Gamry default), \( I_{corr} \) is the corrosion current, \( K = 3272, EW \) is the equivalent weight in g/equiv, \( d \) is the density in g/cm³, and \( A \) is the sample area in cm².

2.4. Corrosion efficiency (CE) calculation.

The CE was calculated from the corrosion current values using the following equation

\[ CE = \frac{i_{corr} - i_{corr}}{i_{corr}} \]  

(4)

where \( i_{corr} \) and \( i_{corr} \) denote the corrosion current densities of Ni–W coatings obtained from the baths without and with additives, respectively.

The calculation of CE from the charge transfer resistance values was performed using the following equation

\[ CE = \frac{R_{ct}}{R_{ct}^0} \]  

(5)

where \( R_{ct} \) and \( R_{ct}^0 \) denote the charge-transfer resistances of Ni–W coatings deposited in the presence and absence of additives in the bath, respectively.

3. RESULTS AND DISCUSSION

3.1. Tafel Measurements. Figure 2 depicts the Tafel polarization curves derived for the Ni–W alloy and Ni–W/OPD and Ni–W/PPD composite coatings. The alloy corrosion parameters extracted from the Tafel curves after fitting with the equivalent circuit (Randles circuit) are tabulated in Table 2. The data obtained from the Tafel measurements provides a clear assessment of the rate of electron transfer within the anodic and cathodic sites, anticipating the stability of coatings when in contact with the corrosive species.\(^{30,31}\) Corrosion potential (\( E_{corr} \)) is a measure of corrosion susceptibility\(^{32}\) or a tendency of the corrosion reaction.\(^{30}\) A higher positive magnitude of \( E_{corr} \) (−116, −118 mV) reported for the additive-assisted alloy matrix composite coatings (Ni–W/OPD and Ni–W/PPD) suggests a very low vulnerability toward corrosion attack compared with that of bare coatings (−380 mV). Relative to Ni–W (153.4 mA/cm²) and Ni–W/OPD (9.22 mA/cm²), a obvious decrease in the corrosion current density (\( I_{corr} \)) is observed for Ni–W/PPD (4.68 mA/cm²), ascertainment the adsorption-blocking action\(^{31}\) of the added additive with the minimal hydrogen evolution reaction (HER).\(^{33}\) The observed decrease in \( I_{corr} \) is in line with the calculated corrosion rate (CR) values. The lowest CR (0.083 mm/year) was recorded for Ni–W/PPD, explicating an exaggerated impediment to the anodic dissolution, i.e., alloy dissolution,\(^{34}\) compared with that of bare (2.85 mm/year) and Ni–W/OPD (0.166 mm/year) coatings. The higher the polarization resistance (\( R_p \)), the higher the anticorrosion property.\(^{35}\) In the current research work, a higher and significant value of \( R_p \) (4963.3 Ω cm²) was attained for Ni–W/PPD compared with that of bare ones (\( R_p \) 203.1 Ω cm²), contributing to the full embodiment of the additive into the alloy matrix interfacial area, mitigating the traverse of corrosive species through the coating and to the substrate. A lower value of \( R_p \) of 2917.4 Ω cm² for Ni–W/OPD compared with that of Ni–W/PPD illustrates the partial embodiment of the additive into the alloy matrix interfacial area, corroborating to its lower corrosion efficiency (CE). The partial/full embodiment of additives into the coverage area of the alloy surface owes to the nature of positional isomeric spacers (ortho and para) and is further discussed in the next section. A smaller value of
porosity density (PD) attained for Ni−W/PPD (3.7%) demonstrates that the addition of PPD into the bath enhanced the formation of fine-grained deposits with higher binding energy between the crystallographic planes. Thus, it is logical to conclude that the well-embedded additive molecules have obstructed the diffusion of aggressive species effectively.

### 3.2. EIS Measurements.

In using EIS to get insight into the adsorption property of employed additives and their role in resisting the electrochemical degradation of coated samples kinetically, i.e., ongoing interfacial reactions, the Nyquist and Bode plots are the most common representations. Nyquist plots of Ni−W coatings obtained in their as-deposited state and with the addition of OPD and PPD in the bath are displayed in Figure 3. The graphs display a single elliptical circle with a different radii, suggesting a one time-constant process corresponding to the charge-transfer mechanism at the interface of the corrosive electrolyte and coatings. In general, for this type of single time-constant process, a widely used Randles circuit is used, which is reported to be the best-fitted electrochemical equivalent circuit (EEC) containing $R_s$, $R_{ct}$, and $CPE_{dl}$ components. The executed equivalent circuit consists of the following elements: $R_s$ is the solution Ohmic resistance that is placed in series with the parallel connection of charge transfer resistance ($R_{ct}$) and constant phase element (CPEdl). The relative radius of the impedance arc accounts for its anticorrosion performance. The longest the diameter, meaning a decrease in the surface area of coatings with the corrosive electrolyte, the superior the corrosion performance. The extracted data from the proposed EEC are presented in Table 3.

Table 3. Parameters of Bare Alloy and Ni−W/OPD and Ni−W/PPD Coatings from the Fitted EEC

| coatings     | $R_s$ (Ω cm$^2$) | $C_{dl}$ (μF/cm$^2$) | $n$ | $R_{ct}$ (Ω cm$^2$) | CE (%) |
|--------------|------------------|---------------------|----|---------------------|--------|
| Ni−W         | 4.58             | 70.46               | 0.82 | 62.06               |        |
| Ni−W/OPD     | 3.97             | 28.07               | 0.90 | 2125.02             | 97.07  |
| Ni−W/PPD     | 4.40             | 22.05               | 0.93 | 3316.71             | 98.12  |

Figure 4. Bode and phase-angle plots of the investigated samples measured in 0.5 M H$_2$SO$_4$ aqueous solutions.

Figure 5. Probability of molecular adsorption of OPD and PPD onto the alloy surface.
−3316.71 Ω cm² in the case of Ni–W/PPD indicates the active role of PPD in the cathodic discharge process or in the reduction of ternary precursors. Furthermore, evidence for this is the lower value of CPEdl (22.05 μF/cm²) and higher value of n (0.93). According to the literature, the CPEdl value signifies the formation of dielectric constant/double layer formation at the interface, while the n value corresponds to the surface homogeneity and the capacitive
nature of the coatings. Capacitance is directly proportional to the area of the capacitor exposed to the corrosive solution. A lower CPE dl value in the case of Ni−W/PPD confirms the effective adsorption of PPD onto the alloy surface, which aids in increasing the thickness of double layer/decreasing the dielectric constant that greatly suppresses the dissolution reaction of metallic coatings (Ni−W). A higher exponent value (n = 0.93) confirms its lower porosity, compactness, and its capacitive nature in defying the penetration of SO4 2− ions. A slightly higher CPE dl value of 28.07 μF/cm2 (Ni−W/OPD) illustrates the emergence of a double layer with lower thickness, depicting the fragmentary adsorption of OPD onto the alloy surface, and a lower n value (0.90) for the same coating represents its loose inner layer and relatively lower capacitive nature, facilitating the flow of corrosive ions through the micropores/cracks. The Ni−W coatings in the as-deposited state resulted in the highest CPE dl value (70.46 μF/cm2) and lowest n value (0.82), indicating the formation of a thin double layer at the interface and high roughness with a very loose inner layer, developing the biggest microcracks/pores. This result suggests the easy diffusion of corrosive species through the coating, which evidences the poorer barrier action (bare one). Impedance data obtained from the EEC reveals that Ni−W coatings obtained in their as-deposited state are the most relegated one compared with other coatings (Ni−W/OPD and Ni−W/PPD). Apparently, quantitative evidence of larger R sq smaller CPE dl, and higher n exponent values for Ni−W/PPD coatings deploys the characteristic role of PPD in the citrate-based Ni−W electrolyte. As seen in Figure 4, the Bode phase plot of Ni−W/PPD displays one wide and broad hump in comparison with that of Ni−W/OPD, which is attributable to its compactness and uniform nature. The Ni−W bare coatings exhibit two time constants, pointing out its highly porous nature, irregular coverage, and adsorption of alloy coatings onto the copper substrate. Among the considered coatings, a higher phase angle (−80°) and a

![Figure 7. Cross-sectional morphology of electrodeposited films: (a) Ni−W alloy, (b) Ni−W/OPD, and (c) Ni−W/PPD.](image)

![Figure 8. Elemental composition of prepared samples: (a) Ni−W alloy, (b) Ni−W/OPD coating, and (c) Ni−W/PPD coating.](image)

![Table 4. Roughness Parameters, Tungsten (wt %) Content, and Crystalline Size Data of Bare and Doped Nanocomposites](data)

| sample name | R a (nm) | R q (nm) | R z (nm) | W (wt %) | crystallite size (nm) |
|-------------|---------|---------|---------|---------|----------------------|
| Ni−W        | 20.60   | 26.40   | 183.61  | 27.18   | 36.1                 |
| Ni−W/OPD    | 19.83   | 24.72   | 174.82  | 32.45   | 23.8                 |
| Ni−W/PPD    | 15.67   | 19.35   | 140.0   | 34.01   | 18.1                 |

![Figure 9. XRD patterns of Ni−W and Ni−W/OPD and Ni−W/PPD composite coatings.](image)
slope of 3.6 are achieved for Ni−W/PPD, demonstrating the capacitive behavior of the electrical double layer in mitigating the passage of aggressive species through the coating and to the substrate surface.53,54 Deviation from the ideal capacitive behavior, i.e., −90°, may refer to the surface inhomogeneity of the formed Ni−W coatings.55 In the current research work, the executed additives possess similar molecular structure but differ in regard to the nature of positional isomeric spacers (ortho and para). A schematic representation of additive adsorption onto the alloy surface is shown in Figure S. Having a keen look at the molecular structures, the adsorption of the OPD additive takes place through oxygen atoms. However, in the case of PPD additive, both oxygen and nitrogen play a synergetic role in the effective adsorption. The concept of chemisorption comes into the picture, which involves a strong interaction through ionic bonds between the adsorbate (organic molecule) and the adsorbent (Ni−W surface). Here, the C=N functional group, where N possesses relatively lower electronegativity and a large number of lone pair of electrons, contributes to the high electronic density.56–58 Additionally, in both cases, π electrons in multiple bonds and aromatic clouds and homo- and heteroatomic multiple bonds like C=O, C=C, and C=N offer a strong coordination with the alloy surface. However, between Ni−W/OPD and Ni−W/PPD, the latter one resulted in a high charge-transfer resistance (3316.71 Ω cm²) and thus in its enhanced corrosion efficiency (95.29%). Here, the positional isomeric spacer plays a crucial role in effective chemisorption and therefore obstructs the corrosion process. In the case of Ni−W/OPD coatings, the additive (OPD) possesses a closer spacer or bonds that lead to ring strain and high steric hindrance, diminishing the adsorption. However, in the case of Ni−W/PPD, as the additive (PPD) possesses a large spacer between two naphthalene rings, it exhibits lower steric hindrance and a lack of the ring strain makes the adsorption predominant. Furthermore, the rapidly adsorbed/intercalated PPD along
with Ni–W ion matrixes forms a new grain that densifies the grain boundary and fills the micropores/cracks during the electrodeposition process, leading to the formation of uniform and bright electrodeposits.

3.3 Surface Morphology. Figure 6 depicts the morphology data of Ni–W alloy coatings fabricated from the electrolytes without and with organic additives (OPD and PPD). For a clear observation, the micrographs of Ni–W coatings are shown in lower and higher magnifications and the calculated grain sizes are mentioned in the corresponding micrographs. Figure 6a indicates that coatings of the as-deposited state show high irregularity with a large-grained surface. Throughout the surface, cluttered micropores were interspersed. Clear grain boundaries with uneven nodules indicate their higher grain size and porosity density (12.2%) (Table 2). The primary cause for these types of crystal defects is hydrogen embrittlement, which extenuates the lateral growth of multiple islands, resulting in incomplete cohesion or discontinuities.59 In contrast, the composite coatings of Ni–W/OPD showed a significant difference in the morphology of the clear and uniform surface with lesser cracks and smaller nodules. Here, the employed additive played the principle role of a diffusing element that intercalates or adsorbs into the alloy matrixes or on the surface of the alloy and provides a larger surface area, reducing the grain size and yielding lesser porosity density (6.3%). A partial decrease in the grain boundary is visualized by the formation of a fine organic layer during the process of electrodeposition. However, the composite coating of Ni–W/PPD displayed a very smooth, compact, and homogeneous morphology with a fewer nodules. Here, the additive PPD acted as a rapidly diffusing element, reducing the surface energy, increasing the nucleation rate, and resulting in a decrease in the defect density1 of Ni–W coatings. The full encapsulation of the organic additive (PPD) into the Ni–W matrixes showed a profound effect on the disappearance of the grain boundary with even lesser porosity density (3.7%). Moreover, the additive helped in the growth of multiple islands laterally, supporting the complete cohesion and suggesting a planar surface with minimal coating defects.

3.4 Cross-Sectional Observation. Concerning the cross section, the morphologies of Ni–W coatings in their as-deposited state and from the baths with added of OPD and PPD are shown in Figure 7. It illustrates that the morphology (Figure 7a) exhibits a more heterogeneous structure with higher inclusions, larger pores, and segregated islands, making the surface very loose. A coarse-grained microstructure with bestowed crystals makes the interface combination feeble, i.e., the adhesion between the Ni–W coatings and Cu substrate becomes worse. One of the possible strategies to lessen the coarsening problem is to decrease the kinetic race between densification and grain growth.60 It was observed that the Ni–W/OPD coating is compact and dense with a good sign of cohesion between the two islands. A partial extenuation in the coarse graining is observed, making the interface combination better compared with that of bare alloy coatings. Here, the added additive helped in controlling the growth of crystalline facets (Ni–W) kinetically through adsorption–desorption interactions.61 Furthermore, the additive molecule reduces the volume of hydrogen bubbles by adsorbing them onto the cathode surface, leading to grain refinement. However, the interface between the adsorbate and the adsorbent is not upto the mark (uneven distribution of facets), making Ni–W alloy coatings less corrosion resistant in comparison with Ni–W/
PPD coatings. Favorably, the Ni–W alloy coatings acquired from the bath containing PPD show a fine planar structure with a good interface combination among the Cu substrate, Ni–W coating, and organic layer. This illustrates that the
strongest adsorption of the PPD additive with crystal planes at high speed rates encouraged the preferred development.59 Apparently, less microcracks, smallest pore size, and absence of coarse grains reflect the significance of the added additive (PPD). Furthermore, the decrease in the volume of H₂ bubbles upon effective adsorption leads to the formation of smooth and compact deposits without any evidence of bulk or interface defects.59 Nevertheless, in all cases, a few scratches were noticed that were formed during the substrate pretreatment process and were inevitable.61

3.5. Elemental Analysis. A semiquantitative elemental analysis of the Ni–W, Ni–W/OPD, and Ni–W/PPD matrix composites was carried out with the aid of EDX, and the corresponding spectra are shown in Figure 8. The obtained spectra illustrate that the elemental contents of Ni–W in their as-deposited state are 72.82 wt % Ni and 27.18 wt % W. As for the composite coating contents, Ni is 67.55 wt % and W is 32.45 wt % for Ni–W/OPD and Ni is 65.99 wt % and W is 34.01 wt % for Ni–W/PPD. A clear observation of an increase in tungsten (wt %) is observed for the alloy coatings deposited from the bath containing additives. In general, the alloy composition principally depends on the transference number (ionic mobility and ionic concentration) at the cathode–electrolyte interface.52 For the Ni–W alloy system, the ionic mobility of the Ni²⁺ citrate complex is faster than that of the WO₄⁻² citrate complex, which results in the lower tungsten wt %. Another factor that regulates the content of tungsten (27.18 wt %) is the evolution of H₂ gas at the cathode–solution interface, as observed in several other reports.63 However, the coatings obtained in the presence of additives (OPD and PPD) resulted in a higher W content, i.e., 32–34 wt %. Previous reports state that electrodeposition of nickel and tungsten ions from the citrate-based electrolytes is kinetically controlled by activation in the case of former one (Ni²⁺) and by diffusion in the case of the latter one (W⁶⁺), i.e., by adsorption or surface coverage process of the cathode.10,44,64,65 Here, the added additive played a key role as a hydrogen suppressor, providing a greater chance for tungsten adsorption at the cathode–solution interface by increasing the bulk metal ion concentration. Another factor that contributes to the further increase in tungsten wt % (Ni–W/PPD) is the increase of the surface activity of W ions compared with that of Ni ions65 aided by the PPD additive during electrodeposition.

3.6. Phase Structure Analysis. Figure 9 shows registered XRD spectra for Ni–W alloy coatings obtained in their as-deposited state and from the plating electrolytes containing OPD and PPD. The spectrum reveals the formation of three prominent peaks at 2Θ angles of 43.9, 50.5, and 74.1° with a preferred grain orientation of (111), (200), and (220) planes of the face-centered cubic (fcc) structure. Among these, the (111) plane is the most preferred one, where Ni–W is present as a single substitutional solid solution66 in which Ni acts as a solvent and W as a solute.67 A popular and well-known Debye–Scherer equation has been implemented to calculate the crystalline size of alloy deposits. The average crystalline sizes of the alloy coatings in the descending order are Ni–W (36.1 nm) > Ni–W/OPD (23.8 nm) > Ni–W/PPD (18.1 nm). Among these, a notably decrease in the crystalline size is noticed in the case of alloy coatings deposited from the PPD (additive)-doped bath. Herein, the added additives act as a crystal modifier that aids the grain growth in a specific direction.68 In comparison with that of the bare one (Ni–W), the appearance of a sharp, intensified peak corresponds to the more crystalline nature.40 Broadening of the X-ray diffraction line is ascribed to the reduction of crystallite size, where the loaded additive molecules into the metal matrixes inhibited the further growth of Ni crystallites by providing more nucleation sites, resulting in grain refinement.69 The highly intensified and sharpened peaks at (111) and (220) were observed for the Ni–W/PPD coating, confirming its highest deposition rate68 and the preferred grain orientation in a specific direction. Another factor that influences the crystalline size of the Ni–W alloy system is the wt % of the tungsten.14 The measured reflection (220) plane intensity is found to be dependent on the tungsten content.63 In the present study, it followed the same trend (Table 4); the (220) plane intensity increases with the increase in wt % of tungsten, resulting in a small crystallite size (Ni–W/PPD). In summary, the XRD spectra revealed that the addition of OPD and PPD into the Ni–W ion solution has not much influenced the peak position, illustrating a similar phase structure with no obvious lattice disorder.40

3.7. Surface Roughness. Precise information on the surface, growth behavior, and roughness of Ni–W alloy coatings has been obtained by atomic force microscopy (AFM). The parameters corresponding to the roughness of the obtained electrodeposits are tabulated in Table 4. By careful observation of the topography (Figure 10a) of the samples, Ni–W coatings in the as-deposited state exhibit large, protruding, globular grains with a maximum height of 183.61 nm. The average surface roughness (Rₚ) and root-mean-square roughness (Rₛ) values of the same are 20.6 and 26.4 nm, respectively. The obtained results posit that the surface shows the evidence of high heterogeneity because of varied deposition rates between the clusters of nucleus and a lack of nuclei during the budding stage of the electrodeposition process, resulting in a nonuniform electrocrystallization.15 The roughness of Ni–W/OPD (Figure 10b) slightly decreased with an average value of Rₚ of 19.83 nm and Rₛ of 24.72 nm. However, the topography displays lesser microcones with a minimal protruding site value of 174.82 nm. This illustrates that the OPD in the bath had partially codeposited into the Ni–W alloy matrix, providing a surface area for the reduction of metal ions and yielding a uniform structure with a reduced Rₚ value of 174.82 nm in comparison with that of the neat composite (Ni–W). On the contrary, the alloy deposits (Figure 11) obtained from the bath containing PPD displayed a smooth topography, resulting from the generation of a conical array of thinner and smaller microcones. This showed strikingly different roughness values of Rₚ of 15.67 nm and Rₛ of 19.35 nm. A considerable decrease in the surface roughness can be visualized with a maximum height of Rₛ of 140.0 nm, which can be ascribed to the full codeposition of the PPD additive into the Ni–W alloy matrixes, and no obvious cracks or defects have been detected, representing the formation of a compact and dense protective film on the alloy surface with a greater surface coverage area. Finally, the coatings with admirable characteristics (shiny look and uniform surface homogeneity) alludes the concomitant goal of the employed additives in the Ni–W ion solution.

3.8. FTIR Analysis. The incorporation of the additive (PPD) in the Ni–W alloy matrixes during electrodeposition is ascertained using FTIR spectroscopy. A comparative analysis of FTIR spectra of the as-synthesized PPD additive (a) and Ni–W alloy matrix loaded with the additive (b) is presented in Figure 12. The absorption peak at 1050 cm⁻¹ can be assigned to the C–N stretching vibration, while the strong absorption
peak between 1500 and 1520 cm\(^{-1}\) corresponds to C\(\equiv\)N stretching vibrations of the benzene ring. The high-intensity band at 1690 cm\(^{-1}\) demonstrates the presence of C\(\equiv\)N (amine group), which ascribes to the formation of coordinate covalent bonding through the adsorption of the additive molecule onto the alloy matrix. Moreover, the appearance of a sharp peak at 3560 cm\(^{-1}\) gives clear evidence of the presence of the OH group, supporting the evidence of adsorption or inclusion of the additive molecule. More specifically, throughout the spectra, a shift of peaks toward higher intensity was observed, concluding the grafting of hydroxyl, amine, and alkene functionalities.

3.9. XPS Analysis. Surface elements play a pertinent role in determining the protection efficiency of metallic coatings. Herein, XPS has been utilized to explore the surface element electronic state and the corresponding adsorbed organic species. Figure 13a displays the wide XPS spectrum of Ni–W/PPD composite coatings, indicating the presence of Ni, W, N, C, and O. The deconvoluted spectra of the above-stated elements are represented in Figures 13b,c and 14a–c. As can be seen in Figure 13b, the Ni 2p\(_{3/2}\) spectrum shows three photoelectron peaks at 852.6, 855.8, and 861.7 eV, corresponding to the metallic nickel (Ni(0)), nickel oxides (NiO) and hydroxides (Ni(OH)\(_2\)), and complex nickel satellite.\(^{43}\) The appearance of a peak at 852.6 eV demonstrates that the added additive (PPD) aided in the reduction of nickel ions (Ni\(^{2+}\)) to metallic nickel (Ni(0)). Nevertheless, the presence of NiO/Ni(OH)\(_2\) ascribes to the formation of the corresponding oxide layer, which is beneficial in increasing its corrosion efficiency (CE, 95.90%). Figure 13c shows the W 4f spectrum having four decomposed peaks. The peak at 31.6 eV is assigned to the metallic tungsten, W(0). Furthermore, the peaks at around 33.7, 35.5, and 37.6 eV correspond to the formation of various oxidation states of tungsten.\(^{33}\) A highly intensified and distinct peak at 31.6 eV illustrates that the additive aided in actuating the reduction process (W\(^{6+}\) to W\(^{0}\)) proficiently. Trace amounts of W\(^{4+}\) and W\(^{6+}\) were also detected, which evidenced the incomplete reduction of tungsten (W\(^{0}\)) during the electrodeposition process.\(^{38}\) The N 1s spectrum (Figure 14a) depicts three distinct fitted peaks located at the binding energies of 397.6 and 399.8 eV. A notable peak at 399.8 eV corresponds to the C\(\equiv\)N (amine) group of the organic species, which is one of the key promoters in binding of the organic molecule onto the alloy surface.\(^{42,69}\) The second peak at 399.0 eV corresponds to the C–N\(\equiv\)C bond of the aromatic ring.\(^{70}\) Finally, a combined peak at 397.6 eV corresponds to the presence of C–N/\(\equiv\)N– (unprotonated), originated from the adsorption of the additive (PPD).\(^{34}\) The decomposed O 1s spectrum (Figure 14b) shows peaks between 529.0 and 534.0 eV. An obvious peak at 530.7 eV corresponds to the O–Ni (W) species that evidences the Ni–W alloy matrices.\(^{51}\) Two prominent peaks at 531.6 and 531.7 eV could be assigned to OH and H\(_2\)O species, respectively.\(^{51,71}\) These species were derived from the aqueous electrolyte during the process of electrochemical deposition, which is inevitable. The appearance of a OH peak further confirms the stronger adsorption of organic species onto the alloy surface. A small peak appearing at lower binding energy (529.6 eV) can be ascribed to the O–C bond,\(^{51}\) which may be originated from the inorganic compounds such as citrates or urea that are used during bath preparation. Additionally, the C 1s spectrum, shown in Figure 14c, had provided some more information about the degree of oxidation. Distinct doublet peaks at 284.0 and 285.5 eV correspond to the C\(\equiv\)C/C\(\equiv\)C bonds of the aromatic ring.\(^{30,72}\) The binding energies of 285.1 and 288.3 eV correspond to the C–N and C–O bonds, respectively,\(^{31,51}\) indicating the adsorption of the organic additive (PPD) during electrodeposition. In sum, the obtained XPS spectrum suggests the chemisorption of the PPD additive onto the alloy surface, and furthermore, the presence of OH and C\(\equiv\)N states indicates the additive–alloy surface interaction.

4. CONCLUSIONS

In conclusion, we used two novel additives (OPD and PPD) as barrier-reinforcing dopants in the citrate-based Ni–W ion solution. Comparative analysis of the barrier effect of neat Ni–W and additive-introduced nanocomposite coatings was performed using Tafel and EIS and further confirmed by FESEM, XPS, AFM, and FTIR. Interface interaction of the adsorbate onto the alloy surface occurred through the sharing of electrons via a dative bond, and it varied based on its positional isomeric spacer. As for the Ni–W/PPD case, a uniformly distributed robust and efficient anticorrosive coating was formed via the dative bond as a result of a decrease in the steric hindrance and the crowding effect, with a larger isomeric spacer, portraying the chemical versatility. The preferred grafting and surface adsorption of functional groups ascribe to the reduction of porosity density (3.7%), as demonstrated by XPS and FTIR techniques. The improved affinity between the adsorbate and the adsorbent (organic molecule and alloy surface) induced by a larger isomeric spacer leads to the formation of a stable chemisorbed organic layer that effectively intercepted the electrolyte diffusion. It is believed that the developed additive (similar in geometry but with varying isomeric spacers) endowed Ni–W alloy coatings with eminent corrosion-resistant property in the simulated corrosive environment and could be a great upliftment to produce other binary or ternary alloy coatings with enhanced robust barrier performance.

AUTHOR INFORMATION

Corresponding Authors

Uppalapati Pramod Kumar — School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China; Department of Chemistry, SRM Institute of Science and Technology, Chennai 603203, Tamil Nadu, India; orcid.org/0000-0003-2354-4548; Phone: +86-18679787033; Email: pramod7147@gmail.com

Tongxiang Liang — School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, P. R. China; Email: liang_tx@126.com

Authors

C. Joseph Kennedy — Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore 641114, Tamil Nadu, India

Raju Nandha Kumar — Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore 641114, Tamil Nadu, India; orcid.org/0000-0001-9801-7318

Jayaraj Prabhu — Department of Chemistry, Karunya Institute of Technology and Sciences, Coimbatore 641114, Tamil Nadu, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03599

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Notes
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