Experimental studies on wear and corrosion resistance of pulse electrodeposited Ni-TiO₂ nanocomposite coatings on AISI 304 stainless steel

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Abstract
Nickel-nano titanium oxide (Ni-TiO₂) composite coatings were developed on stainless steel 304 substrate using pulsed electro-deposition technique. Experiments were carried out employing $L_{27}$ orthogonal array, taking current density, frequency, and duty cycle as prime parameters. Coating characterization was done using FESEM with EDAX and XRD. Applying the Response Surface Methodology optimization method, the optimized values of the parameters were identified as duty cycle, frequency and current density with values of 24%, 10 Hz and 0.6 A cm$^{-2}$ respectively. Vickers micro-hardness, surface roughness, wear resistance and corrosion resistance were measured initially for the as-coated sample. The sample that yielded the optimum parameters was then heat treated for an hour at 400 °C in a closed furnace and quenched in SAE 40 grade oil. Test results of post heat-treated sample produced maximum micro-hardness of 446.45Hv, reduced surface roughness of 0.292 μm, superior wear rate of 3.20E$^{-07}$ mm$^3$ N$^{-1}$·m$^{-1}$ and corrosion protection efficiency of 94.52% of Ni-TiO₂ coating at low frequency, along with enhanced wear and corrosion resistance as compared with the as-coated sample.

1. Introduction

In the last decade numerous researchers have shown much interest on the research of Ni nanocomposite coating by pulsed electrodeposition method, using various metal matrix composite (MMC) coatings, and different substrates for various applications such as automotive shell, supporting column, tableware. Many applications are found to be in the area of energy storage such as interconnect for Solid-Oxide Fuel Cells [1], bipolar plates of proton exchange membrane fuel cell [2], bipolar plates for polymer electrolyte membrane fuel cell [3], current collectors of super capacitors [4], microbial fuel cells [5]. Nanocomposite coating is mainly done for improving the surface properties like micro-hardness, resistance to wear, abrasion, erosion, and corrosion; and also self-lubricating, anti-microbial, anti-scaling, and anti-fouling properties.

Pulsed electro deposition technique is widely used for making parts that find applications like circuit board manufacturing, automobile industries, MEMS, biomedical industries, agriculture and aerospace industries due to versatility of the coatings [6–11]. Many coating methods like Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD), magnetron sputtering, plasma spraying, thermal spraying, electrodeposition, are employed. However the electro deposition technique is found to be versatile [12–16], since it offers uniform coatings, smooth surface, fine grains, enhanced surface properties and extended life of the coated surfaces. This method can also be employed to produce complex surfaces with the advantage of reproducibility.

Researchers have studied various second phase nanocomposite coatings like oxides based TiO₂, ZnO, Cr₂O₃, Al₂O₃, SiO₂, ZrO₂, and carbides based SiC, TiC, and nitrides based BN, TiN, Si₃N₄ [17–22]. Using electro deposition technique the coatings produced by direct current (DC), inclusion of foreign particles into the coatings, optimizing the composition, flow of electric current, pulse plating and pulse reverse plating are the
Surface morphologies of the coatings were examined using Field Emission Scanning Electron Microscope (FESEM).

### 2.2. Experimental procedure

**Samples preparation**

Samples are prepared using stainless steel 304 as the base material. Initially 27 numbers of stainless steel 304 work pieces are taken for the coating process. Electro-deposition coatings of Ni-nano TiO$_2$ were prepared in 300 ml of nickel sulphate bath solution in a glass beaker. Chemicals used for preparing the bath where purchased from Merck brand. Pure nickel plate was used as anode and stainless steel 304 as cathode. A distance of 3 cm [30, 31] is maintained between anode and cathode in the bath. The composition of the bath and operating conditions are given in Table 1.

The schematic diagram in figure 1 explains the setup for the coating process. The sample preparation for coating process is illustrated in figure 2. The procedure adopted for coating is illustrated in figure 3. The optimum voltage was found using trial and error approach and the coating time was calculated using Canning handbook surface finishing technology [32].

**Surface morphology**

Surface morphologies of the coatings were examined using Field Emission Scanning Electron Microscope (FESEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDAX). All chemical composition values are quoted in weight percentage.

The micro-hardness of the nanocomposite coated surface using the sample size of 10 mm diameter and 10 mm height was measured by Vickers micro-hardness instrument with a load of 50 g and five indentations [18, 32] on the surface. The measured values have been tabulated for both as-coated samples and heat treated sample. The X-Ray Diffraction (XRD: Philips X pert Pro) analysis was performed on both samples having the dimensions of 10 mm diameter and 2 mm thickness with Cu K$\alpha$ radiation. The surface roughness was measured using surface profilometer and three readings have been recorded and the values were averaged. Wear test was conducted on coated samples as per ASTM G99 standard using the pin on disk tribometer with an applied load of 20 N, sliding distance of 1000 m, track diameter of 60 mm, and sliding time of 15 min. The test was carried out in room temperature under dry condition.

#### Table 1. Bath compositions and operating conditions.

| Bath composition | Quantity | Operating conditions | Values       |
|------------------|----------|----------------------|--------------|
| NiSO$_4$·6H$_2$O | 260 g l$^{-1}$ | pH | 4.5 ± 0.2 [19] |
| NiCl$_2$·6H$_2$O | 42 g l$^{-1}$  | Temperature (°C) | 55 ± 2 [13] |
| H$_3$BO$_3$     | 36 g l$^{-1}$  | Stirring rate | 400 rpm     |
| Nano-TiO$_2$(dm≤100 nm) | 10 g l$^{-1}$  | Frequency (fHz) | 10, 20, 30  |
| SDS             | 0.1 g l$^{-1}$ | Duty cycle (DC, %) | 10, 20, 30  |
|                 |           | Peak current density (CD, A cm$^{-2}$) | 0.2, 0.4, 0.6 |

In this study, the Ni-TiO$_2$ nanocomposite coating is produced by pulsed electro-deposition technique. From the literature survey, it is inferred that only very few research works have analyzed the electrodeposited Ni-TiO$_2$ nanocomposite coating samples that are further surface hardened by oil quenching. The main aim of this in situ experimental work is to analyze the micro-hardness, surface roughness and properties like wear and corrosion resistance, by studying the Ni-TiO$_2$ composite coated samples that are heat treated at 400 °C [11, 27] for one hour in a closed furnace with rapid oil quenching in SAE 40 grade oil [28]. By using Box-Behnken design in Response Surface Methodology (RSM) [12, 29]; the quadratic models were developed with the help of Minitab software for optimizing the process parameters.

Section 2 describes the experimental details like samples preparation and procedure. Section 3 details the experimental design for optimization and the optimization output. Section 4 unfolds a detailed discussion on the results obtained, regarding the analyses of microstructure, micro-hardness, surface roughness, wear and corrosion resistance for the as-coated and heat treated samples. Section 5 draws the conclusion of the present studies.
A multi-channel electrochemical workstation (CHI-650C, USA) was employed to study the corrosion behavior of as-coated and heat treated samples in 3.5% NaCl solution using three-cell electrode and platinum foil electrode. Saturated calomel is the reference electrode. SS304, prepared as per ASTM G106-89 standard, and coated and exposed in 10 mm diameter area, is the working electrode. The open circuit potential (OCP) were performed in the –300 mV and +300 mV range in NaCl medium, followed by electrochemical impedance spectroscopy (EIS) measurements. EIS testing was performed at the frequency range of 100 kHz to 0.1 Hz with amplitude of 10 mV at the OCP.

Potentiodynamic polarization curve tests were carried out over the range from –300 mV below the OCP to +300 mV above the OCP at a scanning rate of 0.5 mV s⁻¹. The criteria of reactivity of the sample were chosen as the corrosion current that was extrapolated at the corrosion potential using cathodic Tafel extrapolation.
The following formulae were used in pulse plating [23]

\[
\text{Frequency, } f = \frac{1}{T_{\text{on}} + T_{\text{off}}}
\]  
(1)

Where and \( T_{\text{off}} \) are current on time and current off time in seconds respectively.

\[
\text{Duty cycle, } dc = \frac{1}{T_{\text{on}} + T_{\text{off}}} \times 100\%
\]  
(2)

\[
\text{Peak Current Density, } I_p = I_{av} \times \frac{1}{dc}
\]  
(3)

\[
\text{Average Current Density, } I_v = I_p \times dc
\]  
(4)

\[
D = \frac{0.89 \lambda}{\beta \cos \theta}
\]  
(5)

Crystallite dimensions were calculated according to equation (5) by using Debye–Scherrer formula [10] with full width at half maximum (FWHM) values of X-ray diffraction. Here, \( D \) is mean crystallite size, \( \lambda \) is X-ray wavelength (0.15418 nm), \( \beta \) is the corrected peak width at half maximum intensity (FWHM) and \( \theta \) is Bragg diffraction angle.

Using the optimum parameters as obtained from optimization, five numbers of samples were further coated and heated for one hour in furnace at 400 °C, the recrystallization temperature of nickel [27] and suddenly quenched [28] in SAE 40 grade oil for improving the hardness by rapid cooling. The micro-hardness and surface roughness values of these five samples were measured and the average value is determined.

3. Process parameter optimization

3.1. Experimental design

RSM is a widely used technique to optimize process parameters for more number of variables [12]. By using three independent variables, namely, frequency (\( f \)), duty cycle (DC) and current density (CD) at three levels, the Box–Behnken design was used in RSM with 27 experiments. Micro-hardness and surface roughness as output responses with optimized data the wear resistance and corrosion resistance was found. The experimental variables and the corresponding levels are indicated in table 1. The design matrix along with the experimental values is exhibited in table 2.

3.2. Optimization outputs

3.2.1. Effect of process parameters

Experiments were conducted and the quadratic models (6) and (7) were developed by using the experimental inputs in second order polynomial equations and the multi-objective optimization equation was also formed with the help of Minitab software.

The empirical relations of micro-hardness and average surface roughness, with the frequency (\( f \)), duty cycle (D), current density (CD) are expressed as second-order polynomial (regression) equations for framing the response surface using [30]. The model presents high determination coefficients \( R^2 \) of 95.82% for micro-hardness and of 97.18% for surface roughness of the responses. The responses of micro-hardness and average surface roughness were evaluated using the Analysis of Variance (ANOVA) tables 3 and 4.

The regression equation in un-coded units for the microhardness relationship with frequency (\( F \)), duty cycle (DC) and current density (CD) the coating parameters were expressed in the second order polynomial equation (9).

\[
\begin{align*}
\text{Micro-hardness} &= 227.3 + 10.57 F + 3.98 DC - 27.0 CD - 0.4476 F^2 \\
&- 0.1872 DC^2 - 185.6 CD^2 + 0.1662 F^*DC \\
&+ 7.30 F^*CD - 2.40 DC^*CD
\end{align*}
\]  
(6)

As inferred from the ANOVA table 3, the quadratic term frequency had the most influencing parameter contributing 39.11%, followed by the linear term current density of 14.07% impact on the hardness value. The other terms interaction shows that the frequency–duty cycle, frequency–current density, linear term duty cycle, current density, quadratic term duty cycle contributing the hardness with values of 10.78, 8.33, 7.77, 6.90 and 6.84% respectively. High current density and low frequency has formed smaller crystal sizes of 17.86 nm in the coating as found using XRD and this provides increased hardness in the coatings. As per the hall-petch effect, the micro-hardness value was increased with lower frequency and higher amount of current density [13]. The model provides high determination coefficient values of \( R^2 \) and adjusted \( R^2 \) as 95.82% and 93.61% respectively that are higher than the predicted \( R^2 \) value of 90.61%.
The regression equation is expressed, as before, as the second order polynomial equation (7).

Surface roughness = 0.3623 + 0.00479 F + 0.00114 DC – 0.4049 CD
– 0.000302 F^2 + 0.000002 DC^2 + 0.4108 CD^2
+ 0.000163 F*DC + 0.01722 F*CD – 0.01219 DC*CD (7)

The most influencing factors from the ANOVA table 4 shows that the linear term frequency, the interaction term frequency– current density, duty cycle– current density and quadratic term frequency giving 30.27, 29.43, 14.75 and 11.34% respectively for the average surface roughness value. The less influencing factors are from the interaction terms frequency– duty cycle, quadratic term current density, linear term current density and duty

Table 2. Design matrix and experimental values of Ni-TiO2 Nano coating.

| Ex. No. | Frequency (f, Hz) | Duty cycle (DC, %) | Peak current density (CD, A cm⁻²) | Surface Roughness (Ra, µm) | Micro-hardness (Hv) |
|---------|------------------|-------------------|-----------------------------------|---------------------------|--------------------|
| 1       | 10               | 10                | 0.2                               | 0.35                      | 313.69             |
| 2       | 10               | 10                | 0.4                               | 0.34                      | 301.81             |
| 3       | 10               | 10                | 0.6                               | 0.34                      | 272.76             |
| 4       | 10               | 20                | 0.2                               | 0.36                      | 328.64             |
| 5       | 10               | 20                | 0.4                               | 0.31                      | 318.79             |
| 6       | 10               | 20                | 0.6                               | 0.30                      | 249.75             |
| 7       | 10               | 30                | 0.2                               | 0.35                      | 271.47             |
| 8       | 10               | 30                | 0.4                               | 0.29                      | 241.65             |
| 9       | 10               | 30                | 0.6                               | 0.26                      | 204.64             |
| 10      | 20               | 10                | 0.2                               | 0.36                      | 328.92             |
| 11      | 20               | 10                | 0.4                               | 0.37                      | 320.82             |
| 12      | 20               | 20                | 0.6                               | 0.42                      | 305.54             |
| 13      | 20               | 20                | 0.2                               | 0.39                      | 331.32             |
| 14      | 20               | 20                | 0.4                               | 0.37                      | 319.24             |
| 15      | 20               | 20                | 0.6                               | 0.39                      | 312.99             |
| 16      | 20               | 30                | 0.2                               | 0.41                      | 311.6              |
| 17      | 20               | 30                | 0.4                               | 0.37                      | 305.55             |
| 18      | 20               | 30                | 0.6                               | 0.35                      | 272.32             |
| 19      | 30               | 10                | 0.2                               | 0.31                      | 244.64             |
| 20      | 30               | 10                | 0.4                               | 0.35                      | 250.31             |
| 21      | 30               | 10                | 0.6                               | 0.45                      | 248.81             |
| 22      | 30               | 20                | 0.2                               | 0.35                      | 264.49             |
| 23      | 30               | 20                | 0.4                               | 0.36                      | 266.19             |
| 24      | 30               | 20                | 0.6                               | 0.42                      | 260.7              |
| 25      | 30               | 30                | 0.2                               | 0.37                      | 262.22             |
| 26      | 30               | 30                | 0.4                               | 0.40                      | 259.95             |
| 27      | 30               | 30                | 0.6                               | 0.41                      | 250.49             |

Table 3. ANOVA for micro-hardness with frequency, duty cycle and current density.

| Source             | DF | Adj SS | Adj MS | F-Value | P-Value | % Contribution |
|--------------------|----|--------|--------|---------|---------|----------------|
| Model              | 9  | 29439.5| 3271.1 | 43.35   | 0.000   | 95.824         |
| Linear             | 3  | 8835.3 | 2945.1 | 39.03   | 0.000   | —              |
| Frequency(F)       | 1  | 2121.2 | 2121.2 | 28.11   | 0.000   | 6.904409       |
| Duty Cycle(DC)     | 1  | 2389.9 | 2389.9 | 31.67   | 0.000   | 7.779015       |
| Current Density(CD)| 1  | 4324.2 | 4324.2 | 57.30   | 0.000   | 14.07507       |
| Square             | 3  | 14452.5| 4817.5 | 63.84   | 0.000   | —              |
| F*F                | 1  | 12018.4| 12018.4| 159.26  | 0.000   | 39.11934       |
| DC*DC              | 1  | 2103.5 | 2103.5 | 27.87   | 0.000   | 6.846796       |
| CD*CD              | 1  | 330.7  | 330.7  | 4.38    | 0.052   | 1.076413       |
| 2-Way Interaction  | 3  | 6151.6 | 2050.5 | 27.17   | 0.000   | —              |
| F*DC               | 1  | 3313.4 | 3313.4 | 43.91   | 0.000   | 10.78496       |
| F*CD               | 1  | 2560.8 | 2560.8 | 33.93   | 0.000   | 8.335286       |
| DC*CD              | 1  | 277.4  | 277.4  | 3.68    | 0.072   | 0.902924       |
| Error              | 17 | 1282.9 | 75.5   | 4.175781|         | 4.175781       |
| Total              | 26 | 30722.4|        |         |         | 100.00         |

R² = 95.82%  R² (adjusted) = 93.61%  R² (predicted) = 90.61%

The regression equation is expressed, as before, as the second order polynomial equation (7).
cycle, quadratic term duty cycle are 6.37, 3.35, 0.88, 0.49 and 0.06% values respectively. The model presents high determination coefficient values of $R^2$ and adjusted $R^2$ as 97.18% and 95.69%, respectively that are higher than the predicted $R^2$ of 91.76%.

3.2.2. Multiple response prediction for both micro-hardness and surface roughness

From the multi-objective optimization plot shown in figure 4, by giving equal weightage to both outputs with composite desirability of 0.99, the micro-hardness and average surface roughness values predicted the optimized parameters. By using the optimized parameters, conformation test were conducted with frequency, duty cycle and peak current density of 10 Hz, 14% and 0.26 A cm$^{-2}$ as input parameters which produced the output responses of micro-hardness 319.15 Hv and surface roughness of 0.323 μm.

4. Results and discussion

4.1. Microstructure analysis

The experimental results of the coating in this present study are compared with the results of earlier studies performed on Ni-TiO$_2$ nanocomposite coating. The maximum inclusion TiO$_2$ in the coating was achieved at frequency 10 Hz [13]. Using the EDAX spectra of Ni-TiO$_2$ nanocomposite coating, the elements Ni – 86.94%, Ti-7.52% and O-5.53% in weight percentage are present on the surface. From the FESEM image (figures 5(a)–(d)), it is found that the surface morphology of the titanium oxide was densely absorbed at the substrate surface, formed in cauliflower shape [34, 35], and as worms like structure that are visible at 200 nm and 100 nm magnification. The presence of nickel is high due to the higher current density.

4.2. XRD analysis

The XRD plot, in figure 6, shows that amorphous structure was formed and characteristic oxide content was not shown in the as-coated surface. The sample that is heat treated at 400°C and oil quenched also shows the same pattern. However the difference observed is that the heat treated sample matched well with JCPDS–3–65–5537 due to the provision of required thermal energy, but in the case of as-coated sample there is a slight shift observed at 20 angle of 42.5 degree due to the close packing of nanocomposites in the coating, forming the plane of 110 [31]. However both peaks of the coated surface show Ni–Titanium phase (Ni–Ti) presence in the coating, and crystal size has increased with the applied thermal energy. There is no presence of oxygen in the coating as ascertained by EDAX performed to find the oxygen presence along with titanium. The full width at half maximum (FWHM) value for the heat treated surface is higher when compared with as-coated surface. Hence, the crystallite size is also increased in heat treated surface. The average crystal size of the as-coated surface was calculated using Debye–Scherrer formula (equation (5)) as 17.86 nm. This clearly indicates that the formation of crystal size is smaller due to the addition of nucleation sites in Ni electrodeposition coatings [35]. The inclusion of nickel in the coatings was reduced due to inclusion of TiO$_2$ in bath, so smaller sized crystals have been formed.

| Source                  | DF | Adj. SS  | Adj. MS  | F-Value | P-Value | % Contribution |
|-------------------------|----|----------|----------|---------|---------|----------------|
| Model                   | 9  | 0.046966 | 0.005218 | 65.08   | 0.000   | 97.17975       |
| Linear                  | 3  | 0.015295 | 0.005098 | 63.58   | 0.000   | —              |
| Frequency(F)            | 1  | 0.014632 | 0.014632 | 182.47  | 0.000   | 30.27582       |
| Duty Cycle(DC)          | 1  | 0.000237 | 0.000237 | 2.95    | 0.104   | 0.490389       |
| Current Density(CD)     | 1  | 0.000426 | 0.000426 | 5.32    | 0.034   | 0.881458       |
| Square                  | 3  | 0.007105 | 0.002368 | 29.53   | 0.000   | —              |
| F*F                     | 1  | 0.005484 | 0.005484 | 68.39   | 0.000   | 11.34722       |
| DC*DC                   | 1  | 0.000029 | 0.000029 | 1.8     | 0.946   | 0.060005       |
| CD*CD                   | 1  | 0.00162  | 0.00162  | 20.21   | 0.000   | 3.352025       |
| 2-Way Interaction       | 3  | 0.024565 | 0.008188 | 102.11  | 0.000   | —              |
| F*DC                    | 1  | 0.003208 | 0.003208 | 40      | 0.000   | 6.657836       |
| F*CD                    | 1  | 0.014228 | 0.014228 | 177.43  | 0.000   | 29.43988       |
| DC*CD                   | 1  | 0.00713  | 0.00713  | 88.91   | 0.000   | 14.75305       |
| Error                   | 17 | 0.001363 | 0.00008  | 2.820253|
| Total                   | 26 | 0.048329 |

$R^2 = 97.18\%$  
$R^2 (\text{adjusted}) = 95.69\%$  
$R^2 (\text{predicted}) = 91.76\%$
4.3. Micro-hardness analysis

The micro-hardness values of the bare, as-coated Ni-TiO₂ SS304 samples and heat treated Ni-TiO₂ SS304 samples were assessed by using Vickers micro-hardness instrument. Due to low frequency and low duty cycle, the maximum hardness was achieved with maximum inclusion of TiO₂ particles and longer off-time in the pulse plating [13]. The as-coated work piece has shown improved hardness than the bare surface. The increase in hardness is attributed to the following three factors: (i) particle strengthening, (ii) dispersion strengthening and (iii) grain refinement [13]. Due to structural refinement of the grains and smaller crystallite size in the coating, the hardness value has been increased. The absorption of TiO₂ increases the nucleation site, delays grain growth, so falling in the grain size and subsequently increasing micro-hardness of the as-coated surface [31].

The micro-hardness value of bare surface is 250 Hv, and after the Ni-TiO₂ deposition over the substrate the micro-hardness value is increased to 319.15 Hv. In addition, it was discovered that the microhardness increased after post-heat treatment and oil quenching, rising from 319.15 Hv to a high of 446.45 Hv. Due to rapid cooling in oil medium, the particles are packed tightly giving high hardness and also better wear resistant surface.

4.4. Surface roughness analysis

In pulsed electrodeposited Ni-TiO₂ nanocomposite coating, the surface roughness is mainly dependent on the current density and the coating thickness [36]. The surface roughness values were measured and averaged value of three readings at three different locations were determined. The bare, as-coated, and heat treated surfaces produced average surface roughness values of 0.480, 0.336 and 0.292 μm. The inclusion of second phase element TiO₂ nanoparticles had major influences on the roughness values. The average surface roughness value has been decreased for the heat treated sample from 0.336 to 0.292 μm, due to grain refinement that formed the smooth surface; hence the wear resistance was much increased to protect the surface [35]. Since surface roughness value for plain bearing applications must be less than 0.4 μm [26]. On comparison, the value obtained in our experiment for heat treated sample (0.292 μm) is lesser nearly by 13.09% than the as-coated surface. Thus it can be clearly inferred that heat treating the coated part can be a good procedure for plain bearing applications.
4.5. Wear analysis

The morphology of wear tracks for the as-coated and heat treated samples are shown in figures 7(a)–(d) and Tribological properties are highlighted in table 5. The hardness and surface deterioration due to wear of the material had the inverse relationship as per Archards law \[36\]. The worn surface clearly shows that deeper grooves are visible in the as-coated worn surface indicating more amount of material and lesser wear resistance \[37, 38\]. However, the heat treated worn surfaces are having lighter grooves and minimum amount of material has been removed during the test. The weight loss of the as-coated surface is 0.00438 grams and that of the heat
The treated surface is 0.00032 grams (lesser by 0.00406 grams). This lesser weight loss is due to the plastic deformation and high wear resistance to the applied load. Due to the grain refinement, heat treated sample had greater wear resistance than as-coated and bare surface. The average coefficient of friction value of as-coated surface and heat treated surfaces are 0.4509 and 0.2075. The lower the friction coefficient value, the higher is the hardness produced, with smooth surface in heat treated surface. The decrease in the value of friction coefficient is due to plastic resistance of the heat treated surface and reduced area of contact between the mating surfaces. Heat-treated surfaces had lower rates of wear, which led to higher wear resistance being seen from the wear data and making them a viable alternative to hard chromium plating [25].

4.6. Potentiodynamic polarization

The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) data for bare surface, as-coated and heat treated surfaces are given in the table 6. Corrosion parameters like corrosion potential \((E_{\text{corr}})\), corrosion current density \((i_{\text{corr}})\), linear polarization \((R)\), corrosion rate \((r_{\text{corr}})\), and corrosion protection efficiency were calculated from the Tafel plot given in figure 8(a). From seen from the Tafel plot, the curves are formed smoothly for the as-coated and heat treat samples indicating that the surfaces are highly passive to corrosion attack. The corrosion surface protection efficiency is 95.55% and 94.52% for as-coated and heat treated surfaces and this indicates very less porosity in the coated surface. The anti-corrosion property of the coatings is increased due to free from cracks, and the uniformity of the coating is improved with decreased grain size in coating to form passivation [35]. The corrosion current density of the as-coated sample is \(10^{-6} \text{ A cm}^{-2}\); hence the as-coated Ni-TiO\(_2\) surface can be a vital replacement for chromium coatings because of its range from \(10^{-6}\) to \(10^{-7}\) A cm\(^{-2}\) and lesser microhardness value than the chromium coating [39].

\[
\text{Protection efficiency, I.E.} = \frac{i_{\text{corr}} - i_{\text{corr}}}{i_{\text{corr}0}}
\]

Where \(i_{\text{corr}0}\) (in A/cm\(^2\)) represents the current density of corrosion for substrate and \(i_{\text{corr}}\) (in A/cm\(^2\)) for the coating [40].

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**Table 5. Tribological Properties of as-coated and Heat Treated Ni-TiO\(_2\) Composite Coatings.**

| Sample            | Wear loss mm\(^2\) | Specific wear rate \(w_s\) in mm\(^3\)/N-m | Avg. CoF @ 20 N | Wear rate mm\(^3\)/N-m |
|-------------------|---------------------|------------------------------------------|----------------|------------------------|
| Bare surface      | \(4.08125 \times 10^{-6}\) | \(2.0406250 \times 10^{-10}\)              | 0.855348637    | \(4.380 \times 10^{-06}\) |
| As-coated sample  | \(4.92135 \times 10^{-7}\) | \(2.4606742 \times 10^{-11}\)              | 0.450948081    | \(3.265 \times 10^{-05}\) |
| Heat-treated sample | \(3.59551 \times 10^{-8}\) | \(1.7977528 \times 10^{-12}\)              | 0.207333580    | \(3.200 \times 10^{-07}\) |

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**Figure 7.** FESEM images: worn surface of as-coated sample (a), (c); worn surface of heat-treated sample (b), (d).
Table 6. Tafel polarization and Nyquist plot values of bare surface and the Ni-TiO₂ composite coatings.

| Sample            | Corrosion potential $E_{corr}$ (V) | Corrosion current density $i_{corr}$ (A cm⁻²) | Corrosion rate $t_{corr}$ (mil/year) | Charge Transfer Resistance $R_{ct}$ (Ω cm²) | Maximum frequency $f_{max}$ (Ω) | Double Layer Capacitance $C_d$ (Ω⁻¹ cm⁻²) | Corrosion Protection efficiency (%) |
|-------------------|------------------------------------|-----------------------------------------------|-------------------------------------|---------------------------------------------|----------------------------------|------------------------------------------|-------------------------------------|
| Bare surface      | 0.166                              | $2.238 \times 10^{-4}$                       | 65.95                               | 7000                                        | 8000                             | $2.842 \times 10^{-9}$                 | —                                  |
| As-coated sample  | $-0.088$                           | $9.952 \times 10^{-6}$                       | 2.933                               | 1500                                        | 800                              | $1.326 \times 10^{-7}$                 | 95.55                               |
| Heat treated sample | $-0.035$                           | $1.226 \times 10^{-5}$                       | 3.612                               | 45                                          | 26                               | $1.360 \times 10^{-4}$                 | 94.52                               |
4.7. Electrochemical impedance spectroscopy

Since the pores are getting reduced, the corrosion resistance has increased \([33, 36]\) for the as-coated and heat treated surfaces, and grains are refined well due to morphological changes in heat treated sample. As indicated by the surface roughness values, smooth surface is formed in the heat treated sample and this will reduce the corrosion rate by dropping the corrosion sites in it \([18]\). The \(R_{ct}\) values of heat treated surface as against bare surface decline, \((7000 \text{ to } 45)\), which clearly indicates that the semi-circle diameter for bare surface is higher and more protection was given in 3.5% NaCl solution.

From the Nyquist plot figure 8(b), the heat treated surface and as-coated surface had least diameter and medium semi-circle while comparing with bare surfaces, and hence both surfaces have good electrical conductivity and thermal conductivity properties than the bare surface. Due to less corrosion resistance of heat treated sample due to enhanced ion transfer between the coated surface and the corrosion medium \([41]\).

However, from the present experimental results, both as-coated and heat treated surfaces had excellent corrosion resistance and their corresponding values are given in table 7.

![Figure 8.](image)

**Table 7.** Comparison of study results with previous works.

| Alloy            | Substrate       | Hardness, Hv | Avg. CoF | Wear rate mm\(^3\)/Nm | Corrosion rate \(r_{corr}\) (mm/year) | References |
|------------------|-----------------|--------------|----------|------------------------|--------------------------------------|------------|
| Ni               | Copper          | 268          | NA       | NA                     | 0.041                                | [13]       |
| Ni-TiO\(_2\)     |                 | 572          | NA       | NA                     | 0.002                                |            |
| Ni-TiO\(_2\)     | Mild steel      | 348          | NA       | NA                     | NA                                   | [19]       |
| Ni-50\% ZrO\(_2\)-TiO\(_2\) & @\(f=10\) Hz | Mild steel     | 199.14       | NA       | NA                     | 3.750 \(\times 10^{-4}\)             |            |
| As-coated        | SS304           | 319.15       | 0.4509   | 3.265 \(\times 10^{-5}\) | 0.0744                               | Present work |
| Heat-Treated     |                 | 446.45       | 0.2075   | 3.20 \(\times 10^{-7}\) | 0.0917                               |            |
| Ni               | Mild steel      | 316          | 2 – 4 \(\mu m\) | 14.88 \(\times 10^{-9}\) | 0.0153                               | [35]       |
| Ni-TiO\(_2\)     |                 | 387          | 0.1 – 1 \(\mu m\) | 9.1 \(\times 10^{-9}\) | 0.0115                               |            |
| Ni – 550\°C for 2 h | Low carbon steel | 740          | NA       | NA                     | 0.1980                               | [42]       |

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However, from the present experimental results, both as-coated and heat treated surfaces had excellent corrosion resistance and their corresponding values are given in table 7.

5. Conclusion

The nanocomposite Ni-TiO\(_2\) coating has a mixture of cauliflower and worms morphology, as per FESEM images analysis, which confirms uniform distribution of nano TiO\(_2\) particles with the nickel matrix. The EDAX data suggests a maximum inclusion of 13.05% of titanium oxide by weight percentage in the coating.

The microhardness and Corrosion protection efficiencies of the heat treated surfaces were enhanced by 78.58% and 94.55%, Consequently, the surface roughness and the average co-efficient of friction values were reduced by 13.09% and 75.73% than the bare surface.

The above results clearly suggest that Ni-TiO\(_2\) coating of parts and post heat treating them can be the right process for many appropriate industrial applications-like plain bearing parts. Ni-TiO\(_2\) coating and heat treatment can also serve as a viable replacement for hard chromium coating.
Data availability statement

No new data were created or analysed in this study.

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References

[1] Tong Y, Bohm S and Song M 2015 Carbon based coating on steel with improved electrical conductivity Acta J. Nanomed. Nanotech. 3 1041 [https://austinpublishinggroup.com/nanomedicine-nanotechnology/fulltext/ajnn-v3-id1041.php]

[2] Ren Y J, Anisur M R, Qiu W, He J J, Al-Saadi S and Singh Raman R K 2017 Degradation of graphene coated copper in simulated proton exchange membrane fuel cell environment: Electrochemical impedance spectroscopy study J. Power Sources 362 366–72

[3] Stoot A C, Camilli L, Spiegelhauer S A, Yu F and Boggild P 2015 Multilayer graphene for long-term corrosion protection of stainless steel biopolar plates for polymer electrolyte membrane fuel cell J. Power Sources 293 846–51

[4] Ning J et al 2014 High-quality graphene grown directly on stainless steel meshes through CVD process for enhanced current collectors of supercapacitors Sci. China Technol. Sci. 57 259–63

[5] Hsu W-H et al 2017 Characteristics of carbon nanotubes/graphene coatings on stainless steel meshes used as electrodes for air–cathode microbial fuel cells J. Nanomater. 2017 9875301

[6] Vaezi M R et al 2008 Electrodeposition of Ni–SiC nano-composite coatings and evaluation of wear and corrosion resistance and electroplating characteristics Colloids Surf. A 315 176–82

[7] Gyfou P, Pavlatou E A and Spyrellis N Effect of pulse electrodeposition parameters on the properties of Ni/nano-SiC composites Appl. Surf. Sci. 254 5910–6

[8] Kaleicheva I K and Karagouzova Z 2018 IOP Conf. Ser.: Mater. Sci. Eng. 295 012036

[9] Refai M et al 2021 Electrodeposition of Ni–ZrO nano-composite for protecting the agricultural mower steel knifes Chem. Pap. 75 139–52

[10] Bhogal S S, Kumar V, Dhami S S and Pabla B S 2015 Preparation and properties of electrodeposited Ni–TiO2 composite coating J. Electrochem. Sci. Eng. 5 37–45

[11] Cheng, D, Xu W, Hua L, Zhang Z and Wan X 1998 Electrochemical preparation & mechanical properties of amorphous nickel–SiC composites Plating and Surface Finishing 85 61–4

[12] Ataie S A and Zaker A 2019 RSM optimization of pulse electrodeposition of Zn–Ni–Al2O3 nanocomposites under ultra sound irradiation, surface and coatings technology Surface and Coatings Technology 359 206–15

[13] Yilmaz G, Hacp G and Orhan G 2014 Properties of Ni/Nano-TiO2 composite coatings prepared by direct and pulse current electroplating J. Mater. Eng. Perform 24 709–20

[14] Vaezi M R et al 2008 Electrodeposition of Ni–SiC nanocomposite coatings and evaluation of wear and corrosion resistance and electroplating characteristics Colloids Surf. A 315 176–82

[15] Abdel Hamid Z, Refai M, El-kilani R M and Nasr G E M 2021 Use of a Ni–TiO2 nanocomposite coating for replacement of conventional hard chromium Surface & Coatings Technology 371 127535

[16] Kumaravel V, Nair K M, Mathew S, Bartlett J, Kennedy J E, Manning H G, Whelan B J, Leyland N S and Pillai S C 2021 Antimicrobial TiO2 nanocomposite coatings for surfaces, dental and orthopaedic implants Surf. Sci. 361 416–19

[17] Lee C-K 2012 Fabrication, characterization and wear corrosion testing of bioactive hydroxyapatite TiN composites: effect of current density on the structure, mechanical, tribological, and corrosion properties Journal of Asian Ceramic Societies 8 1271–84

[18] Stoot A C, Camilli L, Spiegelhauer S A, Yu F and Boggild P 2015 Multilayer graphene for long-term corrosion protection of stainless steel biopolar plates for polymer electrolyte membrane fuel cell J. Power Sources 293 846–51

[19] Myers H R and Montgomery D C 1995 Concepts, advantages and applications Electrochim. Acta 53 3313–22

[20] Jung A and Venkatesan R 2013 Characterization and optimization of pulse electrodeposition of Ni/nano-Al2O3 composite coatings International Journal of Minerals, Metallurgy, and Materials 20 479

[21] Wang L et al 2006 A novel electrodeposited Ni–P gradient deposit for replacement of conventional hard chromium Surface & Coatings Technology 200 3719–26

[22] Kandeva M, Zagorski M, Nikolov R, Stojanov K, But A, Bojko F, Piteľ J and Vencl A 2022 Friction properties of the heat-treated electroless Ni coatings embedded with c-BN nanoparticles Coatings 12 1006

[23] Ali Mardanifar A M and Soheil M 2021 Wear and corrosion of Co-Cr coatings electrodeposited from a trivalent chromium solution: Effect of heat treatment temperature, Surfaces & Coatings Technology 422 127535

[24] Manoj Samson R, Harshavardhana N, Nirmal R and Ranjith R 2020 Enhancement of ductility and strength in 410 stainless steel through cyclic heat treatment IOP Conf. Series: Materials Science and Engineering 912 032034

[25] Myers H R and Montgomery D C 1995 Response Surface Methodology: Process and Product Optimization Using Design Experiments (New York: Wiley)

[26] Natarajan P, Jegan A and Sankar Ganesh S 2019 Development of numerical model for predicting the characteristics of Ni–SiC nano composite coatings on AISI 1022 substrate Mater. Res. Express 6 085048

[27] Spanou S and Pavlatou E A 2010 Pulse electrodeposition of Ni/nano-TiO2 composites: effect of pulse frequency on deposits properties J. Appl. Electrochem. 40 1325–36
[32] Canning W 2005 The Canning Handbook Surface Finishing Technology, 23rd edn (New Delhi: CBS publishers and distributors)
[33] Prasad C, Srinivasa Rao K and Ramji K 2020 Studies on pitting corrosion of pulsed electrodeposited nanocomposite coating, ICETE 2019, LAIS 2 404–12
[34] Banthia S, Sengupta S, Das S and Das K 2019 Synthesis and characterization of novel Cu, Cu-SiC functionally graded coating by pulse reverse electrodeposition Appl. Surf. Sci. 467–468 567–79
[35] Shao W, Nabb D, Rennie N, Sherrington I, Fu Y qing and Luo J 2012 Mechanical and anti-corrosion properties of TiO₂ nanocomposite reinforced Ni coating by electrodeposition J. Electrochem. Soc. 159 L671–6
[36] Yuxin W, Cao D, Gao W, Qiao Y, Xunxue J, Cheng G, Gao W and Zhi Z 2019 Microstructure and properties of sol-enhanced Co-P-TiO₂ nano-composite coatings J. Alloys Compd. 792 617–25
[37] Yousef E, Sharafi S and Irannejad A 2018 The structural, magnetic, and tribological properties of nanocrystalline Fe-Ni permalloy and Fe-Ni-TiO₂ composite coatings produced by pulse electro co-deposition J. Alloys Compd. 753 308–19
[38] Saad S, Boumerzoug Z, Helbert A L, Brisset F and Baudin T 2020 Effect of TiO₂-Nanoparticles on Ni electrodeposition on Copper Wire Metals 10 406
[39] Benea L, Danailaa E and Celis J-P 2014 Influence of electro-co-deposition parameters on nano-TiO₂ inclusion into nickel matrix and properties characterization of nanocomposite coatings obtained Materials Science & Engineering A 610 106–15
[40] Prasad C, Koon a, Vemuri R, Ramana V V and Srimukkas R 2022 Effect of duty cycle variation on Nickel electrodeposits at 10 Hz frequency Chemical Data Collections 41 1–7