Research Article

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Electroless Ni–P–TiO_2 Nanocomposite Coatings for Enhanced Durability and Saltwater Corrosion Protection of Jet Ski Engine Components

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ABSTRACT

Jet ski engine components operate in aggressive marine environments where prolonged saltwater exposure accelerates corrosion and mechanical degradation, leading to reduced service life and high maintenance costs. This study investigates the development and performance of electroless (Nickel - Phosphorus - Titanium oxide) Ni–P–TiO_2 nanocomposite coatings as a protective surface modification for mild steel components. The coatings were produced using an optimized electroless plating bath incorporating nano-sized TiO_2 particles into the Ni–P matrix to refine grain structure, reduce porosity, and enhance passive film stability. Surface morphology and composition were examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), while phase structure was analyzed via X-ray diffraction (XRD). Mechanical performance was evaluated through microhardness testing, and corrosion resistance was assessed using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3.5 wt% % NaCl solution to simulate saltwater exposure. The incorporation of TiO_2 nanoparticles produced a dense, uniform coating with improved adhesion to the mild steel substrate. EIS measurements indicated significantly higher polarization resistance, confirming superior long-term corrosion protection. These improvements are attributed to the barrier effect of well-dispersed TiO_2 nanoparticles, which impede chloride ion ingress and stabilize the passive layer. The results highlight that electroless Ni–P–TiO_2 nanocomposite coatings present a cost-effective and high-performance strategy for extending the operational life of mild steel jet ski engine components in harsh saltwater environments.

Keywords: Surface engineering; Nanocomposite coating; Jet ski engine components; Electroless Ni–P–TiO_2 coating.

1. INTRODUCTION

Marine leisure vessels, such as jet skis, subject metal parts to one of the most severe operating conditions: cyclic wet/dry, high chloride, oxygenated salty water, cavitation, and mechanical impact. The mild steel of many small engine components is especially susceptible to pitting, general corrosion, and fatigue-assisted degradation under such conditions, which reduces the service life and increases the maintenance expenses of marine sports equipment. Recent reviews and surveys have shown that the problem of protecting steel in coastal/estuarine service is not appreciably reduced. At the same time, there continues to be considerable industry interest in compact, inexpensive protective systems for small marine engines (Nazari *et al.* 2023; Pedrizzetti *et al.* 2023; Gül *et al.* 2023; Alhamad *et al.* 2023).

Electroless nickel–phosphorus (Ni–P) coatings are commonly used in corrosion and wear protection due to the easy generation of uniform pin-hole-free films, good adhesion, and property-tunable nature through heat treatment or alloying (Alhamad *et al.* 2024; Biplab *et al.* 2023). Systematic efforts over the past 5 years have been employed to tailor electroless Ni–P bath chemistry, phosphorus content, heat-treatment schedules, and bath-additive concepts to enhance the performance against corrosion in a NaCl solution that is used to mimic seawater. Extensive reviews reported here indicate that Ni–P continues to be the material of choice in the design of corrosion protection in applications that require conformal coating and moderate hardness.

This phenomenon of ceramic nanoparticles dispersion in the Ni–P matrix (i.e., Ni–P nanocomposite coatings) has become a promising means to improve hardness, wear properties, and corrosion resistance at the same time. TiO_2 enjoys a strong position amongst reinforcing particles because of its chemical stability, low price, and multifunctional nature (e.g., it acts as a dispersed particle in enhancing barrier and porosity reduction properties, among other functions, while appropriately modified, it can provide photocatalytic or self-healing properties that hinder biofouling and crevice corrosion). Since 2020, several experimental studies and reviews have been published, demonstrating improvements in microhardness, the formation of a finer grain structure, and significant increases in polarization resistance resulting from the co-deposition of TiO_2 with

Ni–P (Shozib *et al.* 2021; Oppong *et al.* 2022; Liangshuai *et al*. 2021).

Recent experimental papers have shown that loadings and dispersion processes for TiO_2 (e.g., sol-enhanced addition, surfactant-assisted dispersion, ultrasonic stirring, and electrochemically-assisted deposition) are crucial: bad dispersion results in agglomeration and a poorer performance. At the same time, the homogeneous nano-filling improves the barrier effect and the mechanical interlocking with the Ni–P matrix (Saravanan *et al.* 2020; Fayyad *et al.* 2019; Jensen *et al.* 2023; Sui *et al.* 2022). Recent studies over the last 3 years provide best practice process windows, demonstrating that the size of the TiO_2 particles, their surface functionalisation, and bath hydrodynamics play a significant role in the incorporation efficiency and the resulting electrochemical behaviour.

Electrochemical examination: Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in 3.5 wt. % NaCl is still today the mainstream approach to saltwater performance assessment. Recent EIS studies suggested Ni–P–TiO_2 nanocomposites are capable of imparting significantly higher charge-transfer and pore resistances compared with Ni–P, in agreement with the decreased corrosion current densities, and retarded localised attack. Several papers in recent times also incorporate long-term immersion, cyclic polarization, and accelerated cavitation/erosion tests to simulate the realistic marine service and to demonstrate the enhanced life performance of Ni–P–TiO_2 coatings developed on steel substrates (Avinandan *et al*. 2023).

Besides the single particle types addition, composite hybrid strategies (e.g., TiO_2 with graphene derivatives, CeO_2, ZrO_2, or other oxides) have been studied too to combine the action of the products to block chloride transport collaboratively and to improve the mechanical strength; also in this case, such a multipartite approach gave excellent results at the laboratory level last years. Comparative investigations show that when evaluated using availability, cost, and environmental friendliness, TiO_2 is still a strong candidate in the context of marine recreational uses.

From the point of view of materials engineering, two mechanisms account for the enhanced saltwater performance of the Ni–P–TiO_2 coatings: (1) a physical barrier/ceasing effect —homogeneous dispersal of TiO_2 as nanoparticles fills micropores and tortuously extends diffusion pathways for both chloride ions and oxygen, effectively elevating polarization resistance; and (2) microstructural refinement — TiO_2 stimulates refinement of Ni–P grain morphology and results in a more compact deposit that impedes localized breakdown. These mechanisms have been corroborated with SEM/EDS, XRD, and microhardness measurements in recent experimental works.

Practical applications of engine components for jet skis must address issues related to adhesion, thermal stability, and compatibility with mating parts and oil. Pre-treatments, interfacial layers, and annealing are examined with electroless Ni–P composites on low-carbon and mild steel, showing that these treatment methods can control the properties of the coatings while maintaining cohesion, adhesion, and toughness of coatings and their corrosion resistance. The modelling of coupled tribological and electrochemical degradation is of particular significance for engine components subjected to sliding contact and cavitation. In this study, the analysis was carried out under representative operating conditions, namely a cobalt-based counter face sliding at 0.5 $m \cdot s^{-1}$, a contact dimension of 0.7 cm, and a tribological energy input in the range of 0–195 GPa·m (Avinandan *et al*. 2023).

Table 1: Chemical composition and operating conditions of electroless bath

Component / Parameter	Chemical / Condition	Concentration	Purpose
Nickel source	$NiSO_4 \cdot 6H_2O$	25–30 g/L	Source of Ni^{2+} ions
Reducing agent	$NaH_2PO_2 \cdot H_2O$	20–30 g/L	Reduces $Ni^{2+} \rightarrow Ni$, introduces P
Complexing agent	Sodium citrate	20–30 g/L	Prevents Ni^{2+} precipitation
Nano-additive	TiO_2 nanoparticles (anatase, 20–50 nm)	5 g/L	Improves hardness & corrosion resistance
Surfactant	Sodium dodecylbenzenesulfonate (SDBS)	0.2 g/L	Dispersion of nanoparticles
pH	Adjusted with HCl / NaOH	4.8–5.2	Control's deposition rate & quality
Temperature	–	88 ± 2 °C	Optimal Ni–P–TiO_2 deposition
Deposition time	–	90 min	Target thickness ~12–15 µm
Agitation	Magnetic stirring	Continuous	Prevents TiO_2 sedimentation

Although encouraging laboratory findings, some problems persist. Long-term field data under real marine operating cycles are scarce for many of the Ni–P–TiO_2 formulations. At the same time, scale-up issues such as control of agglomerates, bath stability, and reproducibility of incorporation rates have yet to be solved for industrial applications. New holistic literature reviews demand standardisation in testing matrices, i.e., longer immersion times, mechanical-electrochemical coupling, and actual exposure to real seawater to

compare studies more effectively and speed up the transfer of results to the industry (Uysal *et al.* 2019).

In the present work, mild steel jet ski engine parts were coated with electroless Ni–P–TiO_2 nanocomposite coatings, and the dispersion of TiO_2 and the nanometric distribution were optimized. In addition, the mechanical (microhardness, adhesion, wear resistance) and electrochemical behaviour potentiodynamic polarization, EIS) of the micro and nanocomposite coatings were analysed in 3.5wt. % NaCl. The study extends development on recent process improvements (sol-enhanced and electrochemically assisted deposition). It aims to link laboratory performance metrics to marine sport engine parts by incorporating combined wear–corrosion testing and adhesion testing. In the following sections, the experimental protocol is described and the comparison of the experimental results with those for conventional Ni–P coatings is presented, before a mechanistic discussion and recommendations for marine recreational applications.

2. EXPERIMENTAL DETAILS AND PROCEDURE

Substrates comprised mild steel coupons showing the following composition: ~0.1–0.2 wt% C, balance Fe (25 × 25 × 3 mm). The electroless plating bath comprised a nickel salt of $NiSO_4 \cdot 6H_2O$ (25–30 g L^{-1}) as the nickel source, a reducing agent of $NaH_2PO_2 \cdot H_2O$ (20–30 g L^{-1}), a complexing agent of sodium citrate (20–30 g L^{-1}), and nano-additives of TiO_2 nanoparticles (anatase, 20–50 nm, 5 g L^{-1}), with sodium dodecylbenzene sulfonate (0.2 g L^{-1}) for dispersion. The pH was fixed at 4.8–5.2 using dilute HCl and/or NaOH, and the bath temperature was kept at 88 ± 2 °C under constant magnetic stirring to prevent the sedimentation of TiO_2. Before deposition, the steel coupons were polished stepwise with 240 to 1200 grit emery papers, ultrasonically degreased in acetone, rinsed with deionized water, and acid-etched in 10 wt% HCl for 30 s to strip off surface oxides. A fraction of the bath solution was sonicated for 30 min to disperse TiO_2 nanoparticles before being added to the main bath. Deposition times were 90 min, resulting in a coating thickness of about 12–15 µm. The coated specimens were washed with cold water, dried with warm air, and postdeposited by annealing at 300 °C for one h in nitrogen to enhance the hardness and adhesion. SEM-EDS investigated the surface morphology and elemental composition of the films, and XRD characterized the phase of the movie. Microhardness with a Vickers indenter using a 100 g load and adhesion with the pull-off test were determined according to the standard procedure. According to the ASTM G31 standard, immersion corrosion test was conducted on the developed samples. The coated substrates were rinsed with deionised water, cleaned with acetone and deionised water consecutively. Initial weight of the substrates was measured using weighing machine with the accuracy of 1 mg. Then, the substrates were dried and immersed in 3.5 wt.% of NaCl solution at room temperature for 25 days. The substrate was cleaned, drained and the weight loss was determined at the end of every 5-day interval (5, 10, 15, 20, and 25 days). Control or comparison samples were uncoated steel and conventional Ni–P coatings made under the same conditions. The specifics of the bath composition and operating conditions are given in Table 1. The schematic structure can be seen in Fig. 1.

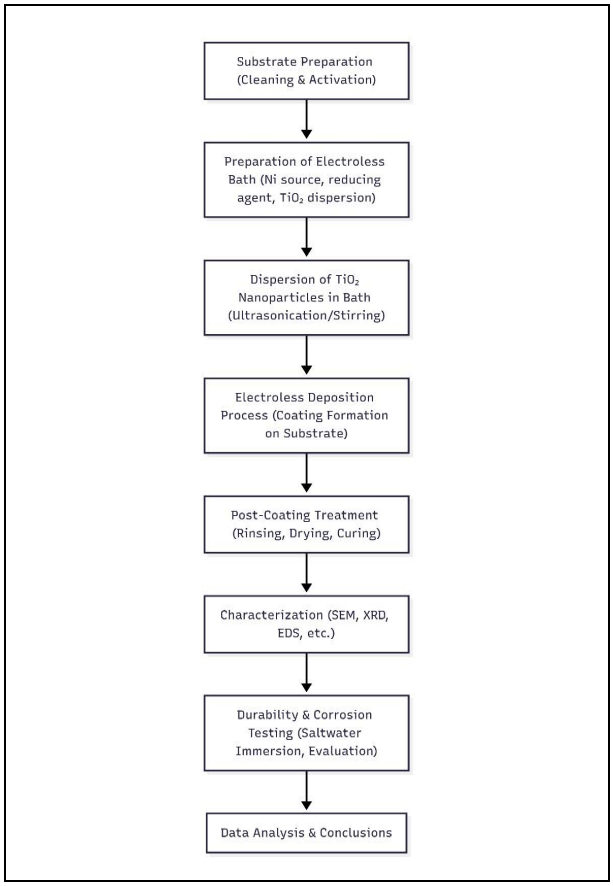

Fig. 1: schematic diagram of electroless Ni-P-TiO_2 nanocomposite coatings

3. RESULTS AND DISCUSSION

3.1 Deposition Rate

Deposition rate is a key parameter for the electroless Ni–P–TiO_2 coating processes because it directly affects the coating thickness, uniformity, and functional properties. Deposition rate (µm h^{-1}) was measured by coating the thickness in terms of micrometers and then dividing by the deposition time in this study. The Ni–P–TiO_2 coatings exhibit an average deposition rate of ~8.0–10.0 µm h^{-1} as a function of TiO_2 nanoparticle loading and bath parameters. Deposition rate was slightly increased by incorporation of 5 g L^{-1} of TiO_2 nanoparticles as compared to the conventional Ni–P coatings (deposition rate ~7.2 µm h^{-1}). Such

enhancement is related to the catalytic function of TiO_2 particles, which serve to nucleate the nickel deposition further. SEM studies have been conducted, and results revealed that the microstructure of coatings with TiO2 became denser in nature, due to the higher deposition rate.

Nevertheless, high amounts of TiO_2 loading (>7 g L^{-1}) in the previous tests resulted in a reduction of the deposition rate owing to the aggregation of the particles and, thus, the blocking of the permeation of nickel ions through the solution toward the substrates. The effect of nano-additions to the electroless baths enhanced nucleation up to an optimum concentration, and then mass transfer constraints limited the efficiency of deposition. In addition, the preserved pH (4.8–5.2) and bath temperature (88 ± 2 °C) were necessary to maintain a uniform deposition rate. Any deviation from these values led to uncontrollable deposition, demonstrating that the autocatalytic reaction was susceptible to process conditions. Generally, the optimized bath composition using TiO_2 nanoparticles obtained the trade-off between deposition rate, coating density, and surface finish, necessary for the corrosion protection of structures in the marine environment.

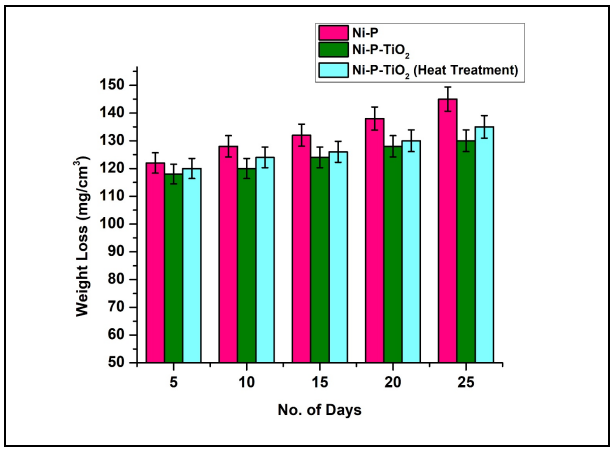

Fig. 2: The weight loss of the substrate subjected to the immersion corrosion test

3.2 Corrosion Test

The immersion corrosion test results clearly demonstrate the superior performance of Ni–P–TiO_2 nanocomposite coatings compared to plain Ni–P, as shown in Fig. 2. After 25 days of saltwater exposure, the Ni–P coating exhibited the highest weight loss of approximately 145 mg/cm³, reflecting its limited corrosion resistance. In contrast, the Ni–P–TiO_2 nanocomposite coating showed a markedly lower weight loss of about 130 mg/cm³, confirming that the incorporation of TiO_2 nanoparticles enhances the barrier properties of the coating and effectively reduces corrosion attack. The heat-treated Ni–P–TiO_2 coating displayed a slightly higher weight loss (~134 mg/cm³) than the as-deposited nanocomposite, likely due to microstructural changes such as crystallization or increased porosity induced during heat treatment. Nevertheless, its performance remained significantly better than that of plain Ni–P. A similar trend was observed at shorter immersion times: at 5 days, Ni–P, Ni–P–TiO_2, and heat-treated Ni–P–TiO_2 exhibited weight losses of ~122, ~117, and ~119 mg/cm³, respectively. These findings establish that Ni–P–TiO_2 nanocomposite coatings provide enhanced durability and superior saltwater corrosion resistance, thereby offering a promising protective solution for jet ski engine components operating in aggressive marine environments.

3.3 Surface Morphology

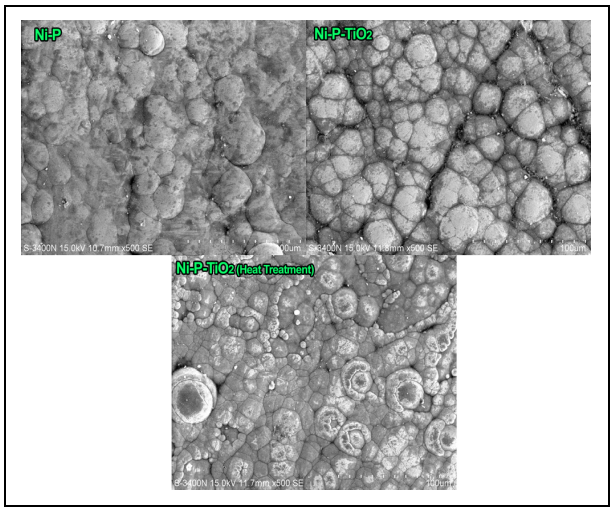

Fig. 3: Surface Morphology of Ni-P, Ni-P-TiO_2

The surface morphology of coatings, as depicted in Fig. 3, SEM micrographs indicate that there is notable variation after the addition of TiO_2 nanoparticles and calcination. The deposited Ni–P coating has a relatively rough and nodular surface and non-uniform distribution, which might provide specific crack initiation and local corrosion in an aggressive situation. The surface is denser and compact, featuring TiO_2 nanoparticles, and exhibits a nodular shape characteristic of Ni–P–TiO_2. This refinement indicates a better structural integrity and fewer defects, and directly results in higher adhesion, higher toughness, and better resistance to crack propagation. However, compared to the N–P–TiO_2 coating after heat treatment, it exhibits an obviously irregular or coarse morphology with larger voids and pit-like structures. These structural changes may be ascribed to relaxation of applied stress and agglomeration of particles during thermal treatment, causing premature and localized loss of coating coherence and increased susceptibility to brittle fracture and pitting corrosion. These findings demonstrate that the addition of TiO_2 nanoparticles can effectively enhance the coating uniformity and compactness. Still, too high a

heat treatment temperature is detrimental to the microstructural stability of the composite layer.

3.4. Adhesion Test

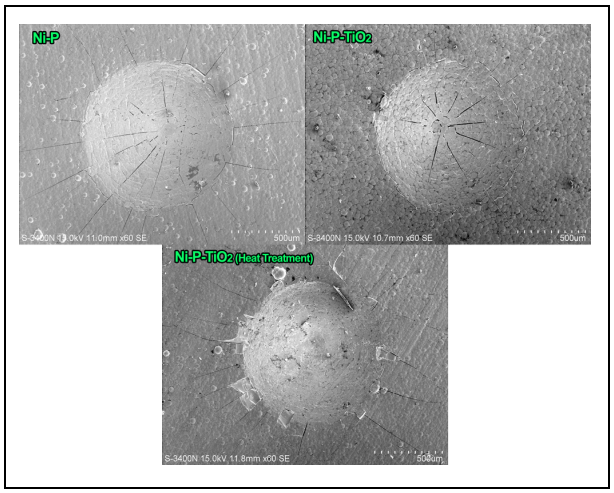

Fig. 4: Adhesion test

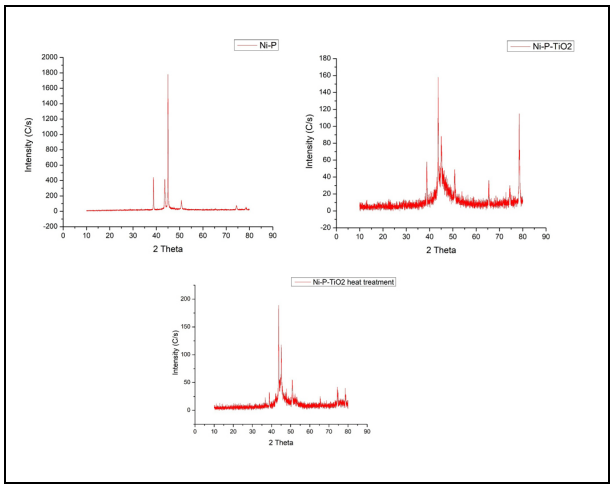

Fig. 5. X-ray diffraction

Adhesion Test – To visualize differences in bonding strength between the coating and substrate, the adhesion test was conducted. See Fig. 4. The Ni–P layer exhibits large radial and circular cracks propagating from the indentation location, indicating a high hardness and brittle fracture mode with medium adhesion strength. In contrast, fewer, shorter cracks were found, and there is almost no spallation or delamination around the indentation edges in the Ni–P–TiO_2 coating. The dense crack network is effectively restrained, which is strong evidence for the adhesion, toughness, and crack propagation resistance. This may indicate that TiO_2 nanoparticle addition enhances interactions with the coating–substrate, decreasing residual stress and improving the coating strength. However, the heat-treated Ni–P–TiO_2 coat exhibits wide radial cracking, localized spallation, and flaking, which mainly occurs near the indentation area, implying a higher propensity to brittle failure and weaker interfacial bonding strength. The failure mechanism shows that the residual stresses induced by the heat treatment are enhanced and the cohesive strength is decreased, making the adhesion inferior to that of the as-deposited Ni–P–TiO_2 coating. In a word, Ni–P–TiO_2 (without heat treatment) exhibits the most desirable adhesion property, and can be considered as the best candidate for protective coating application in seawater conditions.

3.5. X-ray Diffraction

The X-Ray diffraction (XRD) patterns are helpful to understand the phase composition and structural development of the coatings according to Fig. 5. For the Ni–P plating, a broad hump and a sharp peak are observed, mainly accompanied by a very weak and broad signal indicating mostly an amorphous matrix with a certain degree of Ni crystalline phases. When TiO_2 nanoparticles are included (Ni–P–TiO_2), other diffraction peaks are observed that match with TiO_2 (anatase and rutile), indicating the successful coating of the TiO_2 particles into the Ni–P. The sharper peaks also indicate higher crystallinity, which correlates with an enhancement in the hardness and wear resistance of the coatings. Following heat treatment, the diffraction peaks of the Ni–P–TiO_2 coating become stronger and more distinct, indicating that both the Ni–P matrix and the TiO_2 particles received further crystallization. This transformation implies precipitation of Ni_3P and growth of TiO_2 crystallites, which can cause an increase in hardness but may also lead to brittleness and residual stresses. In general, XRD results indicate that introducing TiO_2 is favorable for structure refinement and heat-treatment for increasing crystallinity, but at the expense of toughness.

3.6. Wear and Friction Force

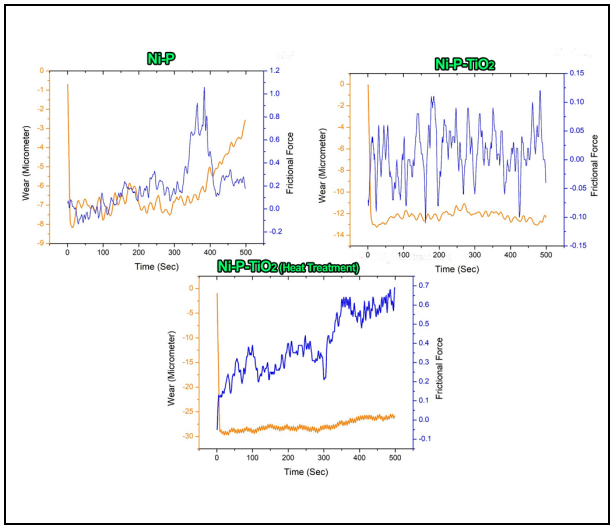

Fig. 6: Wear and friction force

The wear and friction force measurements show differences in the tribological behaviour of the coatings. The wear depth of the Ni–P coating is moderate, which increases slightly with time and fluctuations in the frictional force, as shown in Fig. 6. This response is indicative of its poor resistance to long sliding durations and tendency to initiate micro-cracks. The Ni–P–TiO_2 coating exhibits the least wear rate and a relatively stable, low frictional force throughout the test period. The addition of TiO_2 nanoparticles can remarkably increase the load-bearing capacity and decrease the surface wear as well as improve the wear resistance, due to serving as solid lubricants and strengthening materials dispersed in the Ni–P matrix. The wear depth evolution is increased for the heat-treated Ni–P–TiO_2 coating. It exhibits the highest wear depth evolution with a sudden increase compared to the rest of the samples, and the friction force is also elevated is shown in table 2. This degradation probably results from heat treatment-induced embrittlement and residual stress, which have caused a gradual cohesion failure of the coating and a faster material removal under sliding conditions. Compared to other samples, the Ni–P–TiO_2 nanocomposite-coated sample without heat treatment shows the best tribological properties. It is the most suitable for protecting jet ski engine parts in a seawater environment.

Table 2: Wear rate and average frictional force of all the samples

Samples	Wear Rate (10^{-9}/mm^3 (Nm)$^{-1}$)	Average Frictional Force
Ni-P	53.1	0.58
Ni-P-TiO_2	28.6	0.39
Ni-P-TiO_2 Heat Treatment	9.9	0.18

The overall results indicate that the Ni–P–TiO_2 nanocomposite coating (without heat treatment) provides a combination of structural integrity, adhesion strength, wear resistance, and toughness. Although the Ni–P coating provides modest protection, it is susceptible to brittleness and cracking. Although heat treatment increases crystallinity, it also results in the occurrence of residual stresses and brittleness, which are responsible for the poor adhesion and higher levels of wear. The as-deposited Ni–P–TiO_2 coating is thus found to be the most effective for improving the corrosion resistance and saltwater corrosion resistance of a jet ski engine part.

4. CONCLUSION

This work validated that electroless Ni–P–TiO_2 nanocomposite coatings achieve substantial enhancements in the microstructure, mechanical, and tribological properties compared to the conventional Ni–P coatings. SEM results showed that the presence of TiO_2 nanoparticles results in denser and more uniform surface topography, with fewer sites of defect-prone to localized corrosion. Adhesion test results show that nickel–phosphorous–nano-TiO_2 has better adhesion strength and resistance against crack formation. In addition, the XRD pattern confirmed that the addition of nanoparticles enhanced the crystallinity and microstructure of the coating. Wear and friction test indicated that the lowest wear rate and the most stable frictional condition are achieved for the Ni–P–TiO_2 coating due to the reinforcing and solid-lubricating properties of TiO_2. Contrastingly, the heat-treated Ni–P–TiO_2 resulted in an increase in brittleness and residual stresses on the surface, which degraded adhesion and wear resistance. In summary, the as-deposited Ni–P–TiO_2 nanocomposite coating was found to be the most efficacious for the improvement of durability and saltwater corrosion resistance, thus representing a promising and inexpensive approach to improve the service life of jet ski engine parts while operating in harsh marine environments.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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