

STUDY ON THE MICROSTRUCTURE, PHASE
COMPOSITION, CORROSION RESISTANCE
AND MECHANICAL PROPERTIES OF SELECTIVE
PLATED NANOCOMPOSITE NICKEL COATINGS
WITH EMBEDDED TiO₂

Ivan Rusev[✉], Hristo Skulev, Deyan Veselinov

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Abstract

Nickel and Ni-TiO₂ nanocomposite coatings were deposited on nickel-aluminium bronze by selective electrochemical deposition. TiO₂ nanoparticles below 100 nm were added to a commercial nickel electrolyte to obtain a Ni-TiO₂ composite coating, which was compared with a pure Ni coating. The morphology, phase composition, surface roughness, Vickers microhardness and corrosion behaviour of the coatings were investigated. The Ni-TiO₂ coating showed a compact morphology without defects visible at the optical-microscopy scale. The incorporation of TiO₂ reduced the surface roughness and increased the microhardness from 196 to 215 HV0.2. X-ray diffraction confirmed an fcc Ni matrix and low-intensity reflections attributed to TiO₂. Potentiodynamic polarization in 3.5 wt.% NaCl solution showed a more noble corrosion potential, lower corrosion current density and lower corrosion rate for the Ni-TiO₂ coating. The results indicate that selective plating can produce compact Ni-TiO₂ nanocomposite coatings with improved surface, mechanical and corrosion properties for potential marine applications.

Key words: selective plating, nickel coatings, Ni-TiO₂ nanocomposites, microhardness, corrosion resistance

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Introduction. Marine environments strongly affect the durability and service performance of engineering materials [1–3]. Components used in seawater and coastal conditions are exposed to electrochemical corrosion, cavitation erosion, mechanical wear, and biofouling, which can lead to material degradation and significant economic losses [4–7]. Protective coatings are widely used as an effective and economical approach for improving the corrosion and wear resistance of marine structures, vessels, and equipment [8].

Nickel and nickel-based coatings are commonly employed as protective layers because of their good mechanical properties and ability to form a passive oxide film, which can improve corrosion resistance in aggressive environments [9]. In recent years, metal-matrix nanocomposite coatings have attracted increasing interest because the incorporation of ceramic or oxide nanoparticles can modify the microstructure and improve surface properties. Titanium dioxide (TiO_2) is a suitable reinforcing phase due to its chemical stability, availability, relatively low cost, and corrosion resistance. When incorporated into a nickel matrix, TiO_2 particles may contribute to a smoother and more compact coating morphology, increased hardness, and improved wear and corrosion behaviour compared with pure nickel coatings [10–14].

Selective electrochemical deposition, also known as selective plating, is a useful technique for producing local coatings on electrically conductive surfaces, including components with complex geometry or parts that cannot be treated by conventional bath deposition. The process allows controlled formation of metallic and composite coatings with defined thickness and surface characteristics. Nickel-based coatings produced by selective deposition are of practical interest because they can provide corrosion protection and improved resistance to wear and erosion [15].

Despite the reported advantages of Ni- TiO_2 composite coatings, further study is needed on coatings produced by selective plating on nickel-aluminium bronze substrates, which are relevant for marine applications. In particular, the relationship between coating morphology, phase composition, microhardness, and corrosion behaviour requires clarification.

The aim of the present study is to investigate nickel nanocomposite coatings with embedded TiO_2 particles deposited on nickel-aluminium bronze by selective electrochemical deposition. The morphology, surface roughness, phase composition, microhardness, and corrosion behaviour of the nanocomposite coating are evaluated and compared with those of a pure nickel coating.

Materials and methods. Nickel-aluminium bronze specimens, corresponding to CuAl10Fe5Ni5/ASTM B505 C95500, were used as substrates. The exposed flat working area of each specimen was 4 cm^2 . Before deposition, the substrates were prepared by electrocleaning, electrochemical etching, and surface activation.

Two coating systems were produced by selective electrochemical deposition: a pure nickel coating and a nickel-titanium dioxide nanocomposite coating. The

pure Ni coating was deposited from a commercial acidic Ni 2080 electrolyte supplied by SIFCO ASC. According to the supplier's specification, the electrolyte contained nickel sulphate (< 20 wt.%), nickel formate (< 10 wt.%), and citric acid (< 10 wt.%), with a pH of 2.3.

For the nanocomposite coating, TiO₂ particles with a size below 100 nm were added to the Ni 2080 electrolyte at a concentration of 20 g/L. To improve particle dispersion and limit agglomeration, the suspension was ultrasonicated for 30 min and then maintained under continuous magnetic stirring at 55±1 °C during deposition. Both coatings were deposited potentiostatically at 9 V, with an anode-to-cathode relative speed of 15 m/min. The deposition time was calculated from the ampere-hour requirement necessary to obtain a coating thickness of 20 µm over the defined working area.

The surface morphology and cross-sectional structure of the coatings were examined using an iMet-222 optical microscope equipped with a digital camera and image-analysis software. Surface roughness was measured using a profilometer model DGT-SRT200A, Baxit over a scan length of 5 mm, with a cutoff length of 0.8 mm. The arithmetic mean roughness, R_a , and maximum profile height, R_z , were determined from five repeated measurements for each coating.

The phase composition of the coatings was examined by X-ray diffraction using a TDM-10 diffractometer with Cu K α radiation, $\lambda = 1.5405$ Å. The measurements were carried out in grazing-incidence geometry at an incidence angle of 10° in order to enhance the contribution from the coating layer. The diffraction patterns were processed and phase identification was performed using X'Pert HighScore software.

The microhardness of the coatings was determined by the Vickers method using an HVS-1000 digital microhardness tester. Measurements were performed under a load of 0.2 kgf with a dwell time of 30 s. For each coating, five indentations were made at different locations on the surface, and the results were reported as mean ± standard deviation.

The corrosion behaviour of the coatings was evaluated in naturally aerated 3.5% NaCl solution using a Corrtest CS350 potentiostat/galvanostat. Measurements were performed in a conventional three-electrode cell, with the coated specimen as the working electrode, Pt as the counter electrode, and Ag/AgCl as the reference electrode. The exposed surface area of the working electrode was 1 cm². Before polarization, the open-circuit potential was monitored until a stable value was reached. Potentiodynamic polarization measurements were then carried out, and the corrosion potential, E_{corr} , corrosion current density, I_{corr} , and anodic and cathodic Tafel slopes, β_a and β_c , were determined from the polarization curves. The corrosion rate was calculated from the extracted electrochemical parameters.

Results and discussion. Microstructure and morphology. The surface morphology of the pure Ni coating and the Ni-TiO₂ nanocomposite coating is shown in Fig. 1. Both coatings exhibit a morphology characteristic of selective

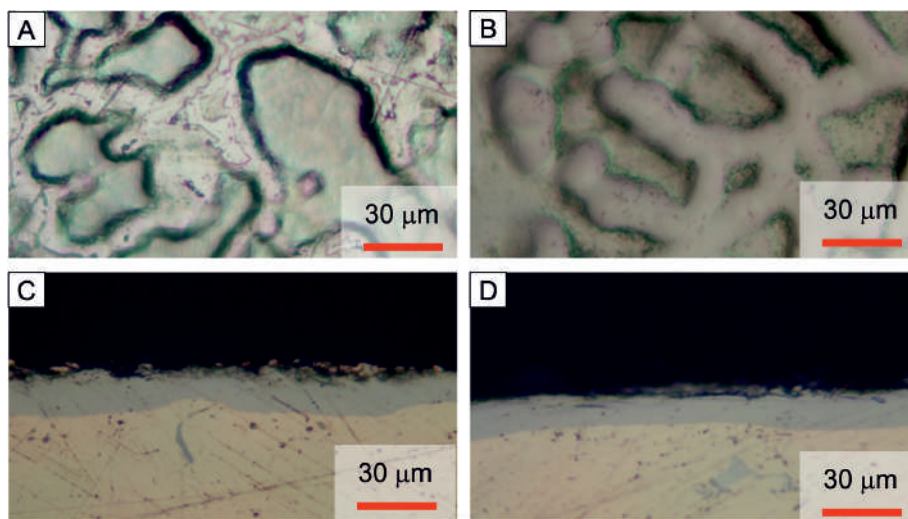


Fig. 1. Optical micrographs of (A) pure Ni coating surface, (B) Ni-TiO₂ nanocomposite coating surface, (C) cross-section of the pure Ni coating, and (D) cross-section of the Ni-TiO₂ nanocomposite coating

electrochemical deposition, where the surface relief is influenced by the relative movement between the anode and the cathode during coating growth.

The surface of the pure Ni coating (Fig. 1A) shows a relatively irregular nodular morphology with more pronounced surface relief and local heterogeneity. In contrast, the Ni-TiO₂ nanocomposite coating (Fig. 1B) exhibits a more uniform and compact surface with smoother morphological features. The incorporation of TiO₂ nanoparticles appears to influence the nucleation and growth behaviour of nickel during deposition, resulting in refinement of the surface structure and suppression of excessive grain growth.

No visible cracks, pores, delamination, or significant particle agglomeration were observed in the nanocomposite coating. The absence of large TiO₂ clusters suggests that ultrasonic dispersion combined with continuous magnetic stirring was effective in maintaining a stable particle suspension during the deposition process. The improved compactness of the Ni-TiO₂ coating may contribute to enhanced barrier properties and improved corrosion resistance.

Cross-sectional observations of both coatings (Fig. 1C, D) reveal continuous and dense deposited layers with an average thickness close to 20 μm. The coatings are well adhered to the nickel-aluminium bronze substrate, and no discontinuities or interfacial defects are visible at the coating/substrate interface. These results demonstrate that selective electrochemical deposition is capable of producing compact and well adherent Ni-based nanocomposite coatings suitable for protective marine applications.

Phase analysis. The X-ray diffraction patterns of the pure Ni coating and the Ni-TiO₂ nanocomposite coating are presented in Fig. 2.

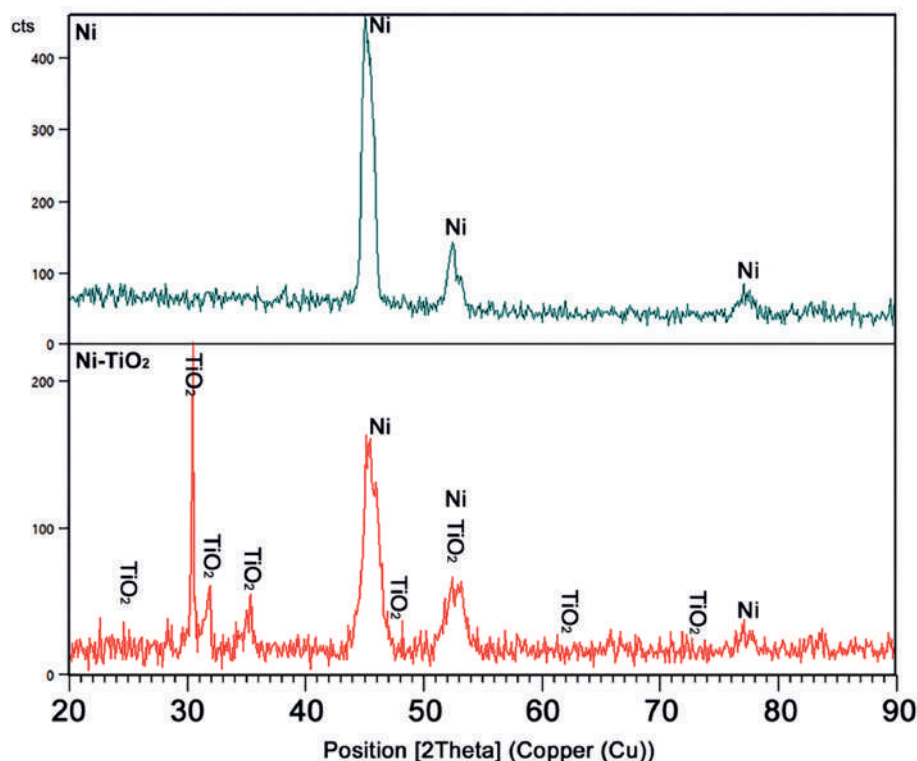


Fig. 2. X-ray diffraction patterns of the pure Ni coating and the Ni-TiO₂ nanocomposite coating deposited on nickel-aluminium bronze

The diffraction pattern of the pure Ni coating is characterized by reflections typical of face-centred cubic nickel. The main peaks are observed at approximately 44.5°, 51.8°, and 76.4°, corresponding to the Ni (111), Ni (200), and Ni (220) crystallographic planes, respectively. The relatively high intensity of the Ni (111) reflection indicates a preferred crystallographic orientation of the deposited nickel layer.

The diffraction pattern of the Ni-TiO₂ nanocomposite coating also shows the characteristic reflections of metallic nickel, confirming that Ni is the dominant crystalline phase in the coating. In addition to the Ni reflections, low-intensity peaks attributed to TiO₂ are observed, which supports the incorporation of TiO₂ particles into the nickel matrix during selective electrochemical deposition. The TiO₂-related reflections are weak and broadened, which may be associated with the nanoscale particle size, the low volume fraction of the oxide phase, and partial overlap with the stronger Ni reflections.

Compared with the pure Ni coating, the Ni reflections in the nanocomposite coating show slightly lower intensity and minor broadening. This behaviour may indicate refinement of the nickel crystallites during deposition in the presence of

dispersed TiO₂ nanoparticles. The embedded particles can act as obstacles to crystal growth, promoting the formation of a finer nickel matrix microstructure.

Surface roughness and mechanical properties. The surface roughness and Vickers microhardness results of the pure Ni and Ni-TiO₂ nanocomposite coatings are presented in Fig. 3. The incorporation of TiO₂ nanoparticles reduced the surface roughness of the nickel coating. The arithmetic mean roughness, R_a , decreased from $1.578 \pm 0.306 \mu\text{m}$ for the pure Ni coating to $0.873 \pm 0.15 \mu\text{m}$ for the Ni-TiO₂ coating. Similarly, the maximum profile height, R_z , decreased from $6.704 \pm 0.45 \mu\text{m}$ to $3.950 \pm 0.40 \mu\text{m}$. These changes correspond to reductions of approximately 45% for R_a and 41% for R_z .

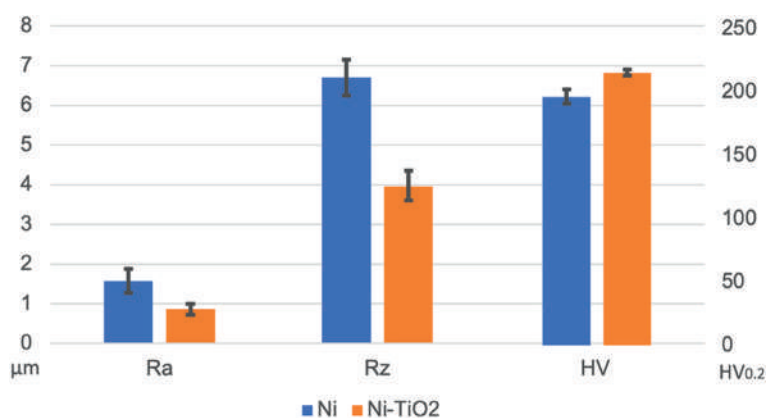


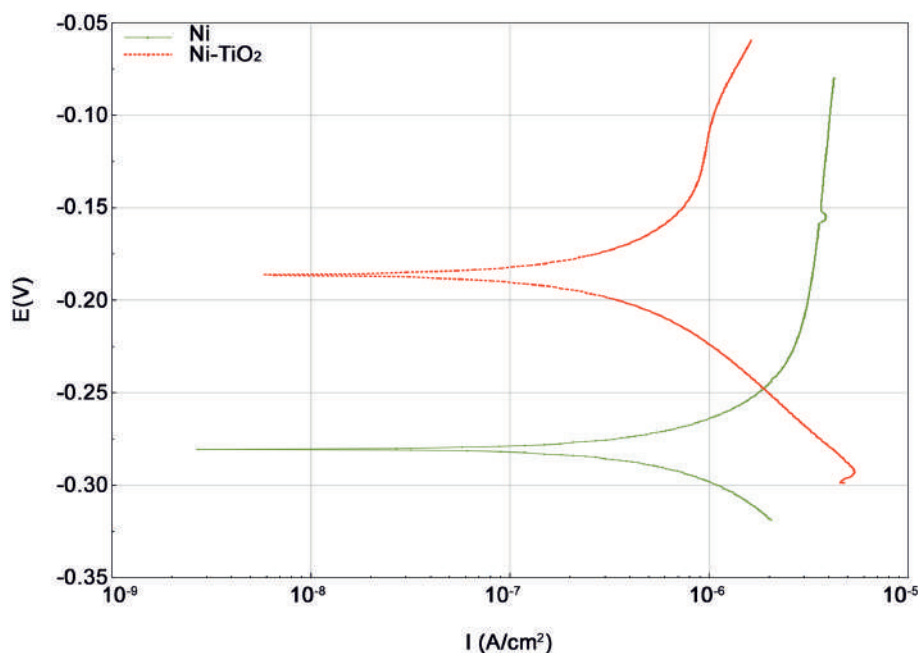
Fig. 3. Surface roughness and Vickers microhardness of pure Ni and Ni-TiO₂ nanocomposite coatings

The lower roughness of the Ni-TiO₂ coating is consistent with the optical microscopy observations, which showed a more uniform and compact surface morphology for the nanocomposite coating. The dispersed TiO₂ particles likely affected the nucleation and growth of the nickel matrix during deposition, promoting the formation of a finer and smoother surface structure.

The Vickers microhardness also increased after TiO₂ incorporation. The microhardness increased from $196 \pm 6 \text{ HV0.2}$ for the pure Ni coating to $215 \pm 3 \text{ HV0.2}$ for the Ni-TiO₂ nanocomposite coating. This moderate increase can be attributed to dispersion strengthening by the embedded TiO₂ nanoparticles, which may hinder localized plastic deformation of the nickel matrix.

Corrosion resistance. The potentiodynamic polarization curves of the pure Ni coating and the Ni-TiO₂ nanocomposite coating measured in 3.5 wt.% NaCl solution, together with the corresponding electrochemical parameters obtained from Tafel extrapolation, are presented in Fig. 4.

The Ni-TiO₂ nanocomposite coating exhibited improved corrosion behaviour compared with the pure Ni coating. The corrosion potential (E_{corr}) shifted from -0.281 V for the pure Ni coating to -0.187 V for the Ni-TiO₂ coating, indicating



	ba (mV)	bc (mV)	i0 (A/cm2)	E0 (V)	Corrosion rate (mm/y)	Residual
Ni	78.289	97.303	1.13E-06	-0.28071	0.012142	4.75E-17
Ni-TiO2	127.19	118.49	6.49E-07	-0.18651	0.0076193	9.65E-12

Fig. 4. Potentiodynamic polarization curves of pure Ni and Ni-TiO₂ nanocomposite coatings in naturally aerated 3.5 wt.% NaCl solution

a more noble electrochemical behaviour after incorporation of TiO₂ nanoparticles. In addition, the corrosion current density (I_{corr}) decreased from 1.13×10^{-6} A/cm² for the pure Ni coating to 6.49×10^{-7} A/cm² for the nanocomposite coating, demonstrating a reduction in the corrosion reaction rate.

The calculated corrosion rate also decreased from 0.0121 mm/y for the pure Ni coating to 0.0076 mm/y for the Ni-TiO₂ coating. This corresponds to an improvement of approximately 37% in corrosion resistance. The improved corrosion resistance is attributed to a denser, more homogeneous Ni-TiO₂ structure. The lower surface roughness and reduced number of microdefects likely limited the penetration of the electrolyte toward the coating/substrate interface.

The anodic and cathodic Tafel slopes of the Ni-TiO₂ coating were also slightly higher than those of the pure Ni coating, suggesting modified electrochemical kinetics associated with the composite microstructure. The incorporation of chemically stable TiO₂ particles may additionally promote the stability of the passive film formed on the nickel surface in chloride-containing environments.

Conclusion. Nickel and Ni-TiO₂ nanocomposite coatings were successfully deposited on nickel-aluminium bronze substrates by selective electrochemical de-

position. Both coatings exhibited dense and continuous structures with good adhesion to the substrate and without visible cracks, pores, or delamination. Compared with the pure Ni coating, the incorporation of TiO₂ nanoparticles resulted in a more homogeneous and compact surface morphology.

X-ray diffraction analysis confirmed that nickel was the dominant phase in both coatings, while additional reflections associated with TiO₂ were detected in the nanocomposite coating, indicating successful incorporation of TiO₂ nanoparticles into the nickel matrix. The incorporation of TiO₂ particles also reduced the surface roughness of the coating, with the R_a and R_z parameters decreasing by approximately 45% and 41%, respectively, which indicates the formation of a smoother surface structure.

The Ni-TiO₂ nanocomposite coating exhibited higher microhardness than the pure Ni coating, with the hardness increasing from 196 HV0.2 to 215 HV0.2. This improvement is attributed to the dispersion-strengthening effect of the embedded TiO₂ nanoparticles and the refinement of the coating microstructure.

Electrochemical measurements performed in 3.5 wt.% NaCl solution demonstrated improved corrosion resistance of the Ni-TiO₂ coating compared with the pure Ni coating. The nanocomposite coating exhibited a lower corrosion current density and corrosion rate together with a more noble corrosion potential, indicating enhanced protective performance in a chloride-containing environment.

The results demonstrate that selective electrochemical deposition is a suitable method for producing Ni-based nanocomposite coatings with improved surface characteristics, mechanical properties, and corrosion resistance for potential marine engineering applications.

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Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre “Acad. A. Balevski”, Bulgarian Academy of Sciences, 67 Shipchenski Prohod Blvd, 1574 Sofia, Bulgaria

e-mails: rusev@ims.bas.bg, skulev@ims.bas.bg, dveselinov@ims.bas.bg