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EFFECT OF TiO_2 ADDITION ON THE MORPHOLOGY, PHASE COMPOSITION AND MICROHARDNESS OF Ni-TiO_2 COMPOSITE COATINGS OBTAINED BY SELECTIVE ELECTROPLATING

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Abstract

Ni-TiO_2 composite coatings were electroplated on AISI 304 stainless steel substrates by selective electrochemical deposition using nickel electrolytes containing 1 wt.% added TiO_2 nanoparticles in the anatase and rutile forms. The coatings were characterized by optical microscopy, X-ray diffraction (XRD) and Vickers microhardness testing and were compared with a pure nickel coating. The addition of TiO_2 nanoparticles affected the deposition behavior and resulting coating thickness. The coating produced with 30 nm anatase TiO_2 exhibited a finer and more homogeneous surface morphology compared with the pure Ni coating. XRD analysis confirmed the face-centered cubic (fcc) structure of Ni and revealed changes in the relative intensities of the Ni diffraction peaks after the addition of TiO_2, with a more pronounced Ni (111) contribution observed for the Ni–TiO_2-A coating. The average microhardness increased from approximately 201 HV0.01 for the pure Ni coating to 354 HV0.01 for the coating produced with 100 nm rutile TiO_2 and to 568 HV0.01 for that produced with 30 nm anatase TiO_2. The results demonstrate that the addition of anatase and rutile TiO_2 nanoparticles affects the morphology, structure, deposition behavior, and microhardness of selectively electrodeposited Ni composite coatings.

Keywords: Ni-TiO_2, nanocomposite coatings, selective electroplating, rutile, anatase

INTRODUCTION

In recent years, metal matrix nanocomposite coatings have attracted increasing interest, as the incorporation of ceramic or oxide nanoparticles can modify the microstructure and improve surface properties. Nickel coatings are often used as protective layers due to their good mechanical properties and their ability to form a passive oxide film, which can improve corrosion resistance in aggressive environments [1-2]. Titanium dioxide (TiO_2) in the two most common crystalline forms (anatase and rutile) is a suitable reinforcing phase due to its chemical stability, availability, relatively low cost and high photocatalytic activity [3]. Selective electrochemical deposition is a useful technique for obtaining localized coatings on electrically conductive surfaces, including components with complex geometries or parts that cannot be processed by conventional bath deposition. The process allows for the controlled formation of metallic and composite coatings with defined thickness and surface characteristics [4-5].

Nickel-based coatings incorporating titanium dioxide particles obtained by selective deposition are of practical interest, as they can provide corrosion protection and improved wear and erosion resistance, combined with photocatalytic activity on the surface. When incorporated into a nickel matrix, TiO_2 particles can significantly improve the mechanical properties of the

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coating, with the Ni-TiO_2 nanocomposite being characterized by a smoother and more compact surface, higher hardness and lower wear rate than pure nickel coating [6-8]. Additionally, nickel shifts the adsorption of titanium dioxide towards the visible light spectrum by introducing intermediate electronic levels into the TiO_2 band gap and suppressing the recombination of electron-hole pairs, which significantly improves the photocatalytic activity of the Ni–TiO_2 composite [9-12]. The addition of TiO_2 nanoparticles improves the surface morphology, reduces the crystallite size and improves the wear resistance and microhardness of the coating. By reducing the grain size of titanium dioxide particles in the nickel matrix, the corrosion resistance of the nanocomposite is significantly improved [13-15].

Despite the reported advantages of Ni-TiO_2 composite coatings, further studies are needed to establish the relationship between the morphology, phase composition and microhardness of coatings obtained by selective deposition on a widely used material with diverse applications in industry, such as steel.

EXPOSITION

Experiment and characterization

Nickel (Ni) and Ni–TiO_2 nanocomposite coatings were formed on AISI 304 stainless-steel samples with a working area of 4 cm^2 by selective electrochemical deposition. Two types of titanium dioxide (TiO_2) were used: anatase (Ni_TiO_2-A) with a particle size of 30 nm, and rutile (Ni_TiO_2-R) with a particle size of 100 nm. The corresponding composite coatings were designated as Ni_TiO_2-A and Ni_TiO_2-R. The calculated target coating thicknesses was 40 μm.

The nickel salt solution used for deposition of the coatings was 2080 supplied by SIFCO Applied Surface Concepts (ASC) with the following chemical composition: CH_2O_2.xNi – 10%, $NiSO_4$ – 20%, $C_6H_8O_7$ – 10% and pH 2.3. To prepare the solutions for deposition of the composite coatings, TiO_2-A or TiO_2-R nanoparticles were added to the nickel salt solution under continuous stirring to obtain a homogeneous suspension with a particle concentration of 1 wt.%. The TiO_2 nanoparticles were dispersed using ultrasound for 15 minutes prior to deposition. Continuous mechanical stirring was subsequently applied during deposition to maintain suspension homogeneity and minimize nanoparticle agglomeration.

Prior to deposition, the substrates were subjected to preliminary surface preparation including electrocleaning, etching and activating. During the selective electrochemical deposition, the temperature of the electrolyte solutions was maintained in the range of 60 ± 1 °C. The coatings were electrodeposited under constant-voltage direct-current conditions. A voltage of 7.0 V was applied. The brush speed was maintained at 15 m/s throughout the deposition process.

The surface topography and microstructure of the coatings were observed on an iMet-222 optical microscope equipped with a camera with a magnification of up to x2000 and software for capturing and processing the results.

The cross-sections were prepared using a low-speed precision cutting machine DTQ-5, then mounted in resin, ground with alumina-based abrasive papers and polished with diamond suspensions to achieve a scratch-free surface suitable for microstructural observation.

X-ray diffraction (XRD) analysis was performed using a TDM-10 X-ray diffractometer equipped with a copper (Cu) anode and Cu Kα radiation with a wavelength of λ = 1.5405 Å. The diffraction patterns were recorded over a 2θ range of 20-90° at an irradiation angle of θ = 10°. The obtained diffraction patterns were processed by background subtraction and normalization and subsequently analyzed using the X'Pert HighScore software package.

The surface microhardness of the coatings was measured by the Vickers method using an HVS-1000 semi-automatic microhardness tester. A load of 0.01 kgf was

applied with a dwell time of 10 s. Three independent measurements were performed for each coating, and the average values were calculated.

Morphology

Figure 1 presents the surface topographies and cross-sections of pure nickel and nickel nanocomposite coatings deposited from electrolytes containing 1 wt.% TiO_2 nanoparticles in the anatase and rutile forms, respectively. The coating obtained without TiO_2 exhibits a relatively rough and heterogeneous surface morphology with clearly distinguishable nodular features. In contrast, the addition of TiO_2 nanoparticles results in a more refined surface morphology, characterized by a finer, denser, and more homogeneous appearance.

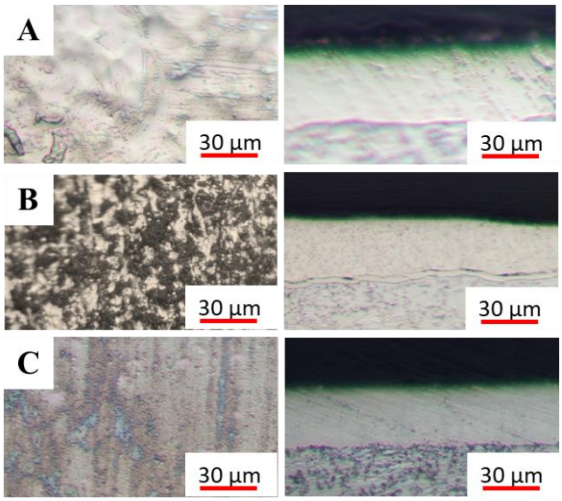


Fig. 1. *Surface and cross-sectional optical micrographs of A) Ni coating and Ni composite coatings with 1 wt.% added TiO_2 nanoparticles: B) N+1%TiO_2-A, C) N+1%TiO_2-R.*

The deposition parameters were selected to obtain a nominal coating thickness of 40 µm. However, for the nanocomposite nickel coatings, an actual thickness of 30 µm was achieved. This reduction in coating thickness may be attributed to inhibition of the electrochemical deposition process caused by the presence of electrically non-conductive ceramic particles in the electrolyte. Consequently, a longer deposition time, expressed in ampere-hours, would be required to achieve the nominal coating thickness of 40 µm.

The cross-sections of both the pure nickel coating and the nanocomposite nickel coatings reveal continuous layers on the stainless steel substrate, without visible macroscopic cracks, defects or delamination at the coating/substrate interface. Since the TiO_2 particles are 30 nm for anatase and 100 nm for rutile, their individual presence or distribution cannot be resolved by the optical microscopy used in this study. Therefore, although the observed changes in surface morphology do not provide direct evidence of TiO_2 incorporation into the nickel matrix, they may be associated with the presence of TiO_2 nanoparticles in the deposition electrolyte.

X-ray diffraction analysis

Figure 2 shows the X-ray diffraction patterns of the pure nickel coating and the nanocomposite nickel coatings deposited from electrolytes containing 1 wt.% added TiO_2 nanoparticles, rutile and anatase, respectively.

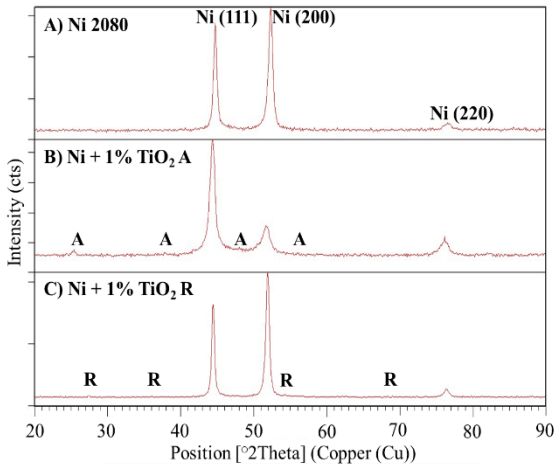


Fig. 2*. X-ray diffraction patterns of A) Ni2080 coating and Ni composite coatings with 1 wt.% added TiO_2 nanoparticles: B) N+1%TiO_2-A, C) N+1%TiO_2-R.*

All samples show the characteristic reflections of face-centered cubic Ni, with the main peaks located at approximately 44-45°, 51-52° and 76-77° 2θ, corresponding to

the Ni (111), (200) and (220) planes, respectively. In the investigated diffraction range, the main peaks of the rutile (TiO_2-R with a main intensity at about 28°) and anatase (TiO_2-A with a main intensity at about 25°) crystalline phases are also clearly observed in the nanocomposite nickel coatings, although with low intensity. The remaining peaks of both TiO_2 forms are significantly less pronounced, which can be attributed to the relatively low TiO_2 concentration and the nanoscale dimensions of the incorporated particles.

For the coating deposited without nanoparticles, the nickel reflections are clearly pronounced, with Ni (111) and (200) having the highest intensity. With the addition of anatase TiO_2-A nanoparticles, the relative intensity of the Ni (200) reflection decreases, and at its base it broadens, while the Ni (111) reflection becomes increasingly dominant. These diffraction data mainly indicate that the addition of TiO_2 changes the crystallographic development of the Ni matrix.

The dispersed TiO_2-A nanoparticles in the electrolyte, given their size of 30 nm, serve as centers for additional nucleation during crystallization during electrodeposition, which may contribute to the refinement of the microstructure and the development of a finer Ni matrix. The inclusion of relatively larger TiO_2-R particles with a size of 100 nm in the nickel matrix also leads to a decrease in the intensity of the nickel peaks, but does not change its crystal structure, as we have the highest intensity of the Ni (111) and (200) crystal lattices.

Microhardness

Figure 3 shows the Vickers microhardness of the pure nickel coating and the nanocomposite nickel coatings deposited from electrolytes containing 1 wt.% added TiO_2 nanoparticles, rutile and anatase, respectively. A clear increase in hardness is observed for the nanocomposite nickel coating with incorporated anatase particles (Ni_TiO_2-A) with a size of 30 nm. This is mainly due to the refinement of the composite structure due to the formation of multiple nucleation centers around the low-sized TiO_2-A particles with a size of 30 nm.

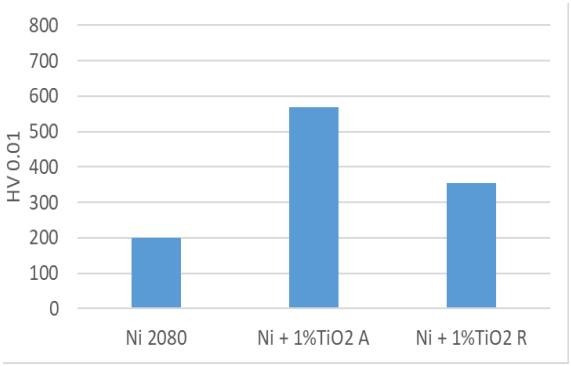


Fig. 3. *Vickers microhardness of Ni2080 coating, Ni composite coatings with 1 wt.% added TiO_2 nanoparticles: N+1%TiO_2-A and N+1%TiO_2-R.*

Based on the presented measurements, the average hardness increases from approximately 201 HV0.01 for the pure nickel coating to approximately 568 HV0.01 for the nanocomposite nickel coating with incorporated anatase particles Ni_TiO_2-A. Besides microstructural refinement, the incorporation of dispersed TiO_2-A ceramic nanoparticles into the nickel matrix can hinder the movement of dislocations and contribute to additional dispersion strengthening.

In the nanocomposite nickel coating with incorporated rutile particles (Ni_TiO_2-R), an increase in microhardness is also reported, with an average microhardness of approximately 354 HV0.01 being measured, with the increase being mainly due to the incorporation of the harder phase of the ceramic TiO_2-R particles into the softer nickel matrix, combined with the dispersion strengthening limiting dislocation motion in the nickel matrix.

CONCLUSION

Selective electroplating was used to successfully deposit Ni-TiO_2 nanocomposite coatings using anatase (TiO_2-A) and rutile (TiO_2-R) nanoparticles. The obtained

coatings were continuous and homogeneous, without visible macroscopic cracks, defects, or delamination at the coating/substrate interface. The results also indicate that adjustment of the deposition parameters and deposition time is required to achieve the target coating thickness in the presence of TiO_2 nanoparticles.

X-ray diffraction analysis confirmed the presence of the characteristic crystalline phases of anatase and rutile in the corresponding nanocomposite coatings, although the TiO_2 reflections exhibited relatively low intensities. This can be attributed mainly to the low concentration and nanoscale dimensions of the TiO_2 particles in the coatings. The addition of TiO_2 also affected the relative intensities of the Ni diffraction peaks, indicating changes in the crystallographic development of the nickel matrix.

The addition of 30 nm anatase nanoparticles resulted in a more pronounced change in the Ni diffraction pattern and may promote additional nucleation during electrodeposition, contributing to the development of a finer Ni matrix.

Both Ni-TiO_2 nanocomposite coatings exhibited increased microhardness compared to the pure nickel coating. The highest average microhardness of approximately 568 HV0.01 was obtained for the coating produced with 30 nm anatase TiO_2 particles, while the coating produced with 100 nm rutile TiO_2 particles also showed a substantial increase in microhardness. The observed strengthening may be associated with a combination of microstructural refinement and dispersion strengthening caused by the incorporated ceramic particles.

Overall, the results demonstrate that the addition of 30 nm anatase and 100 nm rutile TiO_2 nanoparticles affects the morphology, deposition behavior, structure, and microhardness of selectively electrodeposited Ni composite coatings.

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