# EFFECT OF $TiO_2$ NANOPARTICLES ON THE MECHANICAL AND ANTICORROSIVE PROPERTIES OF Zn-Ni COMPOSITE COATINGS

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**Abstract**
In this paper, we are interested in the study of electrochemical, morphological and structural characteristics of the properties of the deposits of Zn-Ni-$TiO_2$ obtained by electrodeposition on the mild steel substrate in a bath of sulfate. The principal aim is to improve the coatings with better properties, by incorporation of titanium oxide, which is a hard compound, chemically stable and irreducible. The characterization of the coatings was carried out by scanning electron microscopy (SEM) and by X-ray diffraction. The morphology of the film surface varies with the concentration of oxide titanium and it was found higher values of microhardness. Electrochemical characterization of the composites had been carried out through potentiodynamic polarization. The results showed that better corrosion resistance with the incorporation of oxide titanium.

**Keywords:** Zn-Ni coating, titanium oxide, electrodeposition, morphology, corrosion

## 1 Introduction

The materials, like humans, need to be well protected from external attack. The main aggressive agents are wear and corrosion. So we took the habit of removing them from this risk by deposits of hard layers and / or protective. The use of coatings for mechanical piece has become widespread, in particular to improve their lifetime.

The elaboration of these coatings involves numerous and varied techniques which make it possible to obtain the wide range of coatings, each having very specific qualities and characteristics. Electrodeposition is one of the most technologically realizable and economically superior techniques for the production of metal matrix composites.

The use of zinc and zinc alloys to improve the corrosion resistance of coated steel sheets has been widely studied due to its importance in industrial contexts. Zn-Ni, Zn-Co and Zn-Fe alloys being the most widely used [1-3].

Zn-Ni alloy is widely used for the corrosion protection of steel, especially in the automotive industry [4]. However, these alloys have low hardness and abrasion resistance with content of nickel, which could be improved by ceramic particle incorporation.

The most important nanoparticles used as deposits are oxides or carbides such as $Al_2O_3$ [5-7], $TiO_2$ [8- 11], $SiO_2$ [12, 13], $ZrO_2$ [7], SiC [7].

$TiO_2$ has been used to improve different metallic and organic coatings. $TiO_2$ with a metallic coating significantly contributes to wear and corrosion resistance, better [8-10, 12]. Vlasa et al. [13] indicated that the porous nanocomposite coatings exhibit higher corrosion resistance when compared to pure Zn coatings and is strongly affected by the $TiO_2$ structure and concentration.

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The zinc metal matrix with $TiO_2$ nanoparticles predominantly shows higher corrosion resistance property due to considerable morphological changes in the deposit and it is confirmed by our previous report on the corrosion behavior of zinc-$TiO_2$ nanocomposite.
In this context, Zn-Ni-$TiO_2$ composite coating on steel was prepared by electrodeposition process. The electrolyte is aqueous solution containing zinc and nickel salts with uniformly dispersed $TiO_2$ nanoparticles. The study also examines the corrosion resistance property of composite with reference to alloy coating.

## 2 Experimental methodologies

### 2.1 Coating preparation

Zn-Ni and Zn-Ni-$TiO_2$ coatings were deposited on mild steel substrates using sulfate bath. The constituents of the bath are illustrated in **Table 1**. The cathode was the mild steel plane and anode was pure zinc (99.99%). The mild steel planes were polished mechanically, degreased in an alkaline solution and treated with HCl (10%). The electrodeposition process was carried out time approximately 30 min under the conditions: T = 30 °C, pH = 3 and density current was J = 3 $A.dm^{-2}$.
The composite deposits were prepared by addition of $TiO_2$ in the electrolyte in a range from 0 to 20 $g. L^{-1}$ and a pitch of 5 $g. L^{-1}$. The nanoparticles are added and stirred for 48 hours to assure good dispersion. The pH of the solution is controlled by the addition of the aqueous HCl or NaOH solutions.

**Table 1** Electrolyte compositions [14]

| Composition | Concentration [$g.L^{-1}$] |
|---|---|
| Zinc sulfate ($ZnSO_4$, $7H_2O$) | 57.5 |
| Nickel sulfate ($NiSO_4$, $6H_2O$) | 52.5 |
| Sodium sulfate ($Na_2SO_4$) | 56.8 |
| Sodium citrate ($Na_3C_6H5O_7$, $2H_2O$) | 56.8 |
| Boric acid ($H_3BO_3$) | 9.3 |

### 2.2 Coating characterization

After the realization of coatings, they are placed in a thermal furnace at 200 °C for 30 minutes to control their adhesion; this method is called thermal shock. It is evident that this object is achieved only if the coating is well adhered to the substrate, the adhesion therefore authorize the quality of the preparation of the surface to be coated and the quality of the coating operation.
The surface morphology of the coatings was examined using a Quanta TM 250 scanning electron microscope (SEM). X-ray diffraction characterization of samples was carried out with a D8 Advance-Brucker uses a Cu Kα line at $\lambda$ = 0.1540 nm in the 2θ ranged from 10° – 95° in steps of 0.02 ° at a scan speed 2 °/min.
Microhardness of the Zn–Ni coatings was measured using Vickers hardness Zwick Roell with 100 g load for 10 seconds.
The corrosion tests were carried out in a neutral aqueous NaCl (35 $g.L^{-1}$) solution, naturally aerated. The test device was composed of a PGZ301 potentiostat and a 1L cell containing electrolytes, into which three electrodes were plunged: the calomel reference electrode saturated in KCl (SCE), the platinum counter electrode and the specimen as the working electrode. In order to determine the corrosion behavior of a specimen immersed in the electrolyte, the curves I (E) are plotted from ± 200 mV versus the corrosion potential using a sweep rate of 10 $mV. min^{-1}$.

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# 3 Results and discussions

## 3.1 Structure and morphology of coating obtained

### 3.1.1 X-ray diffraction

The analyze of x-ray diffraction patterns of the coatings obtained shows the existence of different phases such as: α-phase (Zn) at the preferred orientations (100), (110), (112) and (201). All the detectable peaks could be indexed to hexagonal structure as that are found in the standard reference data (JCPDS No. 00-001-1238), and γ- phase (Ni5Zn21) at orientations (321), (330) (521). All the detectable peaks could be indexed to cubic structure as that are found in the standard reference data (JCPDS No. 00-006-0653). This result is according to the recent researches [15-16]. In the presence of $TiO_2$ corresponding to the tetragonal structure which is consistent with the JCPDS No. 98-000-19161, the intensity of the few peaks changes, this indicates the change in their crystalline size **(Fig.1)**. The peak (330) is the most intense orientation for the Zn-Ni coating.

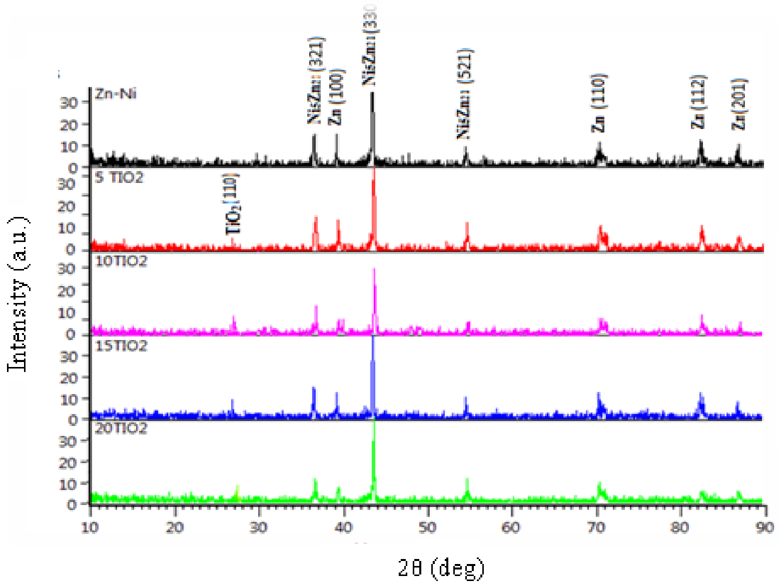


**Fig. 1** XRD patterns of Zn–Ni alloy coatings electrodeposited at different concentrations of $TiO_2$

The grain size of the coatings was determined from X-ray peak broadening by applying the Scherer formula (1) which is well suited to detect a grain size of less than 100 nm [17-18]:

$$D = \frac{0,9\lambda}{\beta cos\theta} \quad (1)$$

where *D* is the grain size, is the X-ray wavelength (λ = 1.5406 Å), β is the full width at half-maximum (FWHM), and θ is Bragg angle position of peak.

For the most intensive peak (330), the grain size for the Zn-Ni and Zn-Ni-15 $g.L^{-1}$ $TiO_2$ coatings is 0.84 nm, 0.63 nm for the two Zn-Ni-5 $g.L^{-1}$ and 10 $g.L^{-1}$ of $TiO_2$ and 0.5 for the Zn-Ni-20 $g.L^{-1}$ $TiO_2$ coating respectively, this indicate that the composite coatings have a size smaller than the grain alloy coatings, the incorporation of $TiO_2$ nanoparticles in the coating has refined crystals. It should be noted that all the particle sizes of the coatings are in nanometric scale, it confirmed the nanocrystalline structure of the composite coatings Zn-Ni and Zn-Ni-$TiO_2$.

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### 3.1.2 Surface morphology

The SEM images show the changes in morphological and structural of the deposits with the addition of the $TiO_2$ in the bath. We also observed the presence of $TiO_2$ in the form of small white dots that are distributed throughout the deposit **Fig. 2**.

It can be clearly seen that the size of the crystals has been reduced by the incorporation of $TiO_2$ from the results of DRX, the small peak at $2\theta = 27.43°$ corresponds to $TiO_2$. It gives evidence of the presence of $TiO_2$ in the coating. The thickness of the coating is 80 μm.

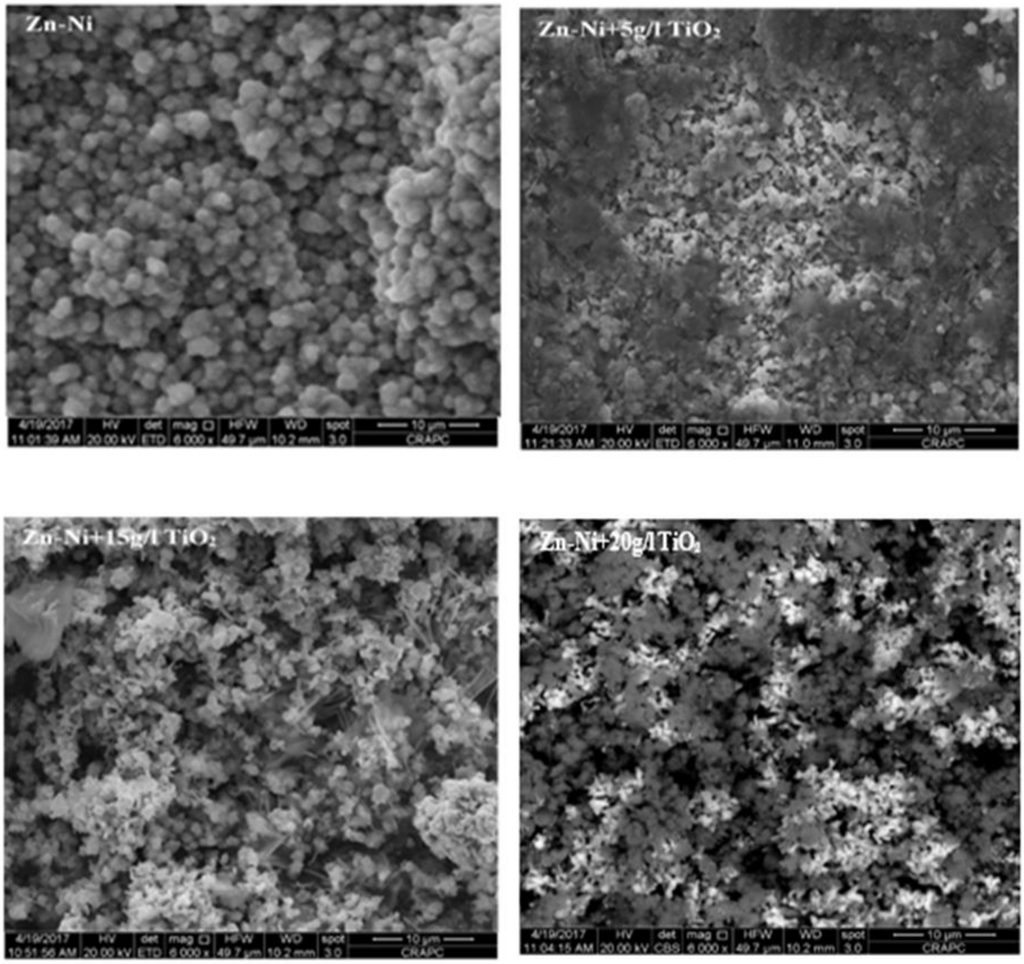


**Fig. 2** SEM image of Zn-Ni deposits with different concentrations of $TiO_2$

### 3.2 Microhardness of Zn-Ni-TiO2 coatings

The compositional variables in microhardness of Zn-Ni alloys have been investigated by various researchers [18-22]. Zn-Ni alloys are harder than pure Zn. In our studies, the microhardness of the coatings increased with the addition of $TiO_2$ nanoparticles. This increase is due essentially to the heterogeneity of the coating, and consequently improves the mechanical properties of the deposits. The results obtained are given in **Table 2.**

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**Table 2** Values of micro-hardness (HV)

| **Concentration of $TiO_2$ (g.L$^{-1}$)** | **Micro-hardness (Hv)** |
|---|---|
| 0 | 106 |
| 5 | 120 |
| 10 | 123 |
| 15 | 144 |
| 20 | 178 |

### 3.3 Corrosion behavior studies of the coatings

The corrosion test of different coating Zn-Ni-$TiO_2$ with the potentiodynamic polarization curves are displayed in **Fig. 3**. The cathodic and anodic tafel slopes βc and βa respectively and the corrosion current densities ($I_{corr}$) are obtained graphically by the intersection of the anodic and cathodic tafel lines extrapolated to the corrosion potential ($E_{corr}$), estimating that the kinetic of electrochemical reactions responsible for corrosion is limited by the charge transfer step, the values of the electrochemical parameters determined from previous polarization curves obtained are presented in **Table 3**.

**Table 3** The electrochemical parameters ($E_{corr}$, $I_{corr}$, βa, βc, $R_p$, $\tau_{corr}$) of the coatings samples in 3.5 % NaCl solution

| **Concentration of $TiO_2$ (g.L$^{-1}$)** | **$E_{corr}$ (mV)** | **$I_{corr}$ (mA.cm$^{-2}$)** | **$\beta_a$ (mV/dec)** | **$\beta_c$ (mV/dec)** | **$R_p$ (Ω.cm$^2$)** | **$\tau_{corr}$ (mm.y$^{-1}$)** |
|---|---|---|---|---|---|---|
| 0 | -1358.20 | 2.69 | 85.0 | -160.3 | 14.52 | 31.55 |
| 5 | -1082.70 | 0.54 | 305.2 | -198.2 | 75.38 | 6.36 |
| 10 | -1151.10 | 0.22 | 143.0 | -157.2 | 206.75 | 2.64 |
| 15 | -1096.10 | 0.01 | 77.1 | -148.9 | 3830.00 | 0.13 |
| 20 | -1263.40 | 0.26 | 2812.1 | -90.6 | 118.81 | 3.04 |

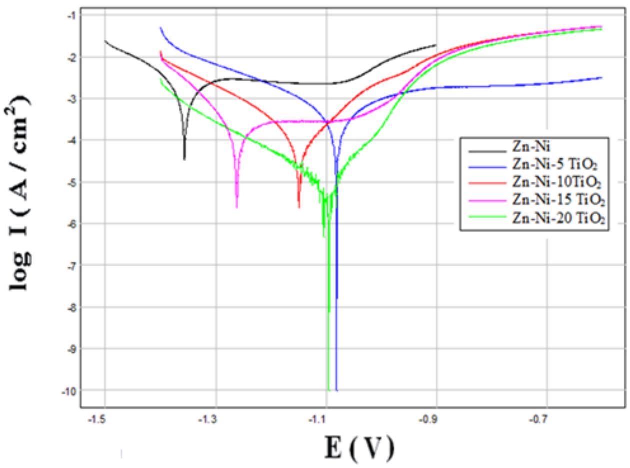


**Fig. 3** Polarizing curves obtained for the alloy coatings in a 3.5 % NaCl solution at different concentrations of $TiO_2$

The analysis of the parameters obtained by the interpretation of the polarization curves revealed less negative Ecorr values (**Fig. 3**), a smaller Icorr value and a larger polarization resistance (Rp)

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value for the nanocomposite coatings. These results indicate that Zn-Ni-$TiO_2$ composite coatings are resistant to corrosion. We can observe that the optimal concentration of $TiO_2$ nanoparticles in the electrolytic is 15 g. L-1. We can say that the incorporation of $TiO_2$ in the coating reducing the corrosion rate (τcorr). An explanation has been given by Saied et al. [9], in which they mentioned that $TiO_2$ nanoparticles changes the structure of the metal deposition, which is most fine, because the nanoparticles provide more nucleation sites and delay the growth of Zn-Ni matrix. $TiO_2$ nanoparticles also fill defects and improve corrosion resistance and hardness.

## 4 Conclusion

The objective of this work was to investigate the effect of $TiO_2$ on the properties of Zn-Ni composite coatings which was deposited on mild steel substrates by electrodeposition from a sulfate bath. From the results, the following conclusions can be drawn:

- X-ray patterns of all the coatings show only the presence of cubic γ-phase $Ni_5Zn_{21}$.
- The size of the crystals was reduced by the incorporation of $TiO_2$, the small peak at 27.43 (2θ) corresponds to $TiO_2$, indicating that these particles refined the crystals.
- Vickers microhardness measurements showed that the incorporation of $TiO_2$ leads to an increase in hardness.
- The optimal concentration of $TiO_2$ nanoparticles in the electrolyte is 15 $g.L^{-1}$; it gives the best corrosion resistance.

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