

# Anti-corrosion Properties and Structural Characteristics of Fabricated Ternary Coatings

O. S. I. Fayomi<sup>a,b</sup> and A. P. I. Popoola<sup>a</sup>

<sup>a</sup>Department of Chemical, Metallurgical and Materials Engineering,  
Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa

<sup>b</sup>Department of Mechanical Engineering,  
Covenant University, P.M.B 1034, Ota, Ogun State, Nigeria  
e-mail: [ojosundayfayomi3@gmail.com](mailto:ojosundayfayomi3@gmail.com), [fayomio@tut.ac.za](mailto:fayomio@tut.ac.za)

In this paper deposition of zinc (Zn) – cobalt (Co) particles and the titanium IV oxide composite (TiO<sub>2</sub>) by electrodeposition in a single electrolyte bath was studied. Zinc coatings modified with cobalt and titanium IV oxide incorporation were produced using optimized process parameters. Morphological and microstructural properties of the fabricated coatings were characterized by an X-ray diffractometer (XRD) and a scanning electron microscope equipped with energy dispersive spectrometer (SEM/EDS). Mechanical characteristics of the coatings were evaluated by a high impact diamond-based Dura Scan micro hardness tester. The corrosion resistance properties were determined with the VA 669 PG STAT 101 using the linear potentiodynamic polarization method. As a result, it was found that the deposition of admixed Zn-Co submicron sized TiO<sub>2</sub> composite particles was successful. A better interfacial interaction was found to exist between the based particulate and the composite. Structural comparison of the deposited coatings with SEM, optical microscope and atomic force microscope images revealed that the homogenous grain structure was formed. Corrosion resistance increased significantly and, in addition, a better micromechanical behavior of the coatings was attained by changing the parameters and content of Co and TiO<sub>2</sub> particulates.

*Keywords: interface, anti-corrosion, reinforcement, structural characterization.*

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## INTRODUCTION

Mild steel is widely used in structural and engineering constructions due to its availability, reasonable cost and physical properties [1–5]. However, it has limited service performance, which is mostly caused by interactions with external media. Main environmental challenges range from chemical to mechanical interactions, depending on the service region. There are usually mechanical interactions between components in contact with each other, which tends to wear materials off. Sometimes, electrochemical responses to the environment gradually lead to lower functionality of the component because of the deterioration of its surface [5–13].

Several coating methods like vapor deposition, painting, thermal spraying, galvanizing, and systems such as zinc–iron, zinc–nickel, zinc–cobalt, chromium, aluminum have been employed over time and recently researchers have come to the verge of developing a system that can combat and strengthen the material used so that it could withstand thermal, chemical and mechanical exposure [14–18].

The discovery of nanocomposite particles for material modifications lately has become very usage for enhancement of binary formations to ternary alloys through electrodeposition. Ceramic composite based depositions are progressively used for various manufacturing applications to offer wear and hardness protection, corrosion resistance, and thermal filling

[1, 19–22]. Some of these ceramics composites have a super bond matrix with ordinary functional coating particulates such as Ni-ZrO<sub>2</sub>, Al-SiC, Ni-PZT, Ni-Al<sub>2</sub>O<sub>3</sub>, Cu-Al<sub>2</sub>O<sub>3</sub>, Zn-Al<sub>2</sub>O<sub>3</sub>, ZnO, TiO<sub>2</sub>, WS<sub>2</sub>, MoS<sub>2</sub>, to mention but a few that have been successfully prepared and fabricated directly or indirectly through the reverse current electrodeposition [23–35].

Co and TiO<sub>2</sub> are in great demand for the generation of particles and composite coatings on steel and alloys with other metals [28, 33]. Zn-Co coatings are reported to have attracted greater interest due to their corrosion protection than Zn coatings; they also have characteristics similar to those of Zn-Ni. Subsequently, the potential advantage of Co addition in bath has been recognized to give resistance to abrasion and improved coating properties [28]. According to [18–20], TiO<sub>2</sub> composite has been effectively co-deposited with Ni, Cu, Ag and Zn. It has numerous potential engineering applications in organic coatings, cells for photovoltaics; it contributes to catalysis, etc. Moreover, TiO<sub>2</sub> with a metallic coating significantly contributes to wear and corrosion resistance, better hardness [18–20, 25, 34].

With the view of the above in the present study we focus on the chemical inducement of Zn-Co-TiO<sub>2</sub>, its microstructural, anti-corrosive and mechanical properties, when formed on mild steel substrates by electrodeposition. The produced coatings were characterized by an atomic force microscope

(AFM), X-ray diffractometer (XRD) and scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Micro hardness was evaluated by the diamond-based Dura Scan micro hardness tester.

## EXPERIMENTAL

### *Preparation of substrates*

Locally sought mild steel coupons of 40 mm x 20 mm x 1 mm were used as substrates and zinc sheets of 30 mm x 20 mm x 1 mm were used as anodes. The nominal composition (in wt. %) of the mild steel plates used is given in Table 1. The cathode was of mild steel coupons and the anode was pure zinc (99.99%). The mild steel specimens were polished mechanically, degreased and immediately water washed.

### *Formation of deposited coatings*

A locally prepared mild steel substrate was activated by dipping it into 10% HCl solution at room temperature for 15 seconds followed by rinsing in distilled water. Analytical grade chemicals and distilled water were used to prepare the plating solution. Prior to plating, the Co and TiO<sub>2</sub> particles were dispersed in the electrolyte, whose composition and parameters are presented in Table 2. The single bath formulation was then heated to about 40°C to provide a stable electrolyte and dissolve nano-particles agglomerate that might be present in the electrolytic solution as a result of a high surface capacity. The bath produced was concurrently stirred as heating lasted for hours before plating. The itinerary bath design is presented in Table 3.

### *Preparation of coatings*

The prepared composite admixed in a single bath after heating for 2hrs and intermittent stirred to obtain clear solution first was obtained by electrolytic deposition over mild steel. Cathodes and anodes were connected to the DC power supply through a rectifier at 2A. Electrodeposition was carried out at the applied voltage varying between 0.5–1.0 V for 15 minutes. The immersion depth was kept constant. Finally, the samples were rinsed in water to wash the salt and oxide solution off the plated samples immediately after the electroplating process.

### *Characterization of coatings*

The surface morphologies of the samples were investigated and the elemental analysis was performed using a TESCAN SEM – EDS and an optical microscope. The EDAX point analysis was used to trace the compositional uniformity, the phase identification of the film formed on mild steel. The topog-

raphy and morphology of the samples surfaces before and after coating were studied by the AFM. The microhardness of the deposit was examined by the equal interval range indentation technique using a diamond-based Dura Scan microhardness tester. The average mean of five point's values with the 20 mm distance was recorded.

### *Electrochemical characterization*

The electrochemical stability behavior of the composite deposited samples was tested in 3.65 wt. % NaCl solution. To study the electrochemical behavior, a conventional three-electrode cell was used, consisting of a saturated calomel electrode (SCE), graphite and coated mild steel ones used as reference, auxiliary, and working electrodes, respectively. The 1.0 cm<sup>2</sup> area of the working electrode was exposed to the solution and the remaining area was covered with epoxy resin, as reported in [5]. The coupons were mounted with resin and the surfaces were made to expose to the medium. The electrochemical measurement was done with an Autolab PGSTAT 101 Metrohm potentiostat/galvanostat. Other accessories were: an electrolytic cell containing 50 ml of an electrolyte, with and without a plated sample, a graphite rod which was an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. The potentiodynamic potential scan was fixed to run from -1.5 V to +1.5 mV, with the scan rate of 0.012 V/s. From the Tafel plots of  $E/I$ , ( $E_{corr}$ ) and ( $j_{corr}$ ) were evaluated.

## RESULTS AND DISCUSSIONS

### *Morphological studies*

Figure 1a shows the surface morphology of Zn-TiO<sub>2</sub> co-deposits. The SEM/EDS image witnesses the dispersed harnessing of TiO<sub>2</sub> nanoparticles in the zinc interface. The surface structure of Zn-TiO<sub>2</sub> composites in the presence of glycine is also visible. The adhesion and fine grains were quite obvious, as stated in our earlier study [5]. The incorporation of TiO<sub>2</sub> and glycine to the electrolyte systematically influences the morphological behavior giving good fine grains as a uniform blend within the matrix. The dispersion also tends to change the result of the bath to give smaller grains. A smaller grain size provides an alteration in the morphological struggle between nucleation and crystal growth [36, 1–2].

It is reasonable to note here that the porous nature of the zinc matrix was minimized, thus providing better morphology due to the composite infiltration into the zinc bath causing adhered and uniform deposition [14, 17–18]. In addition to this, an agglomeration within the zinc matrix might have been expected, but in this case it was different; so it is

**Table 1.** Nominal chemical composition (wt %) of mild steel substrate

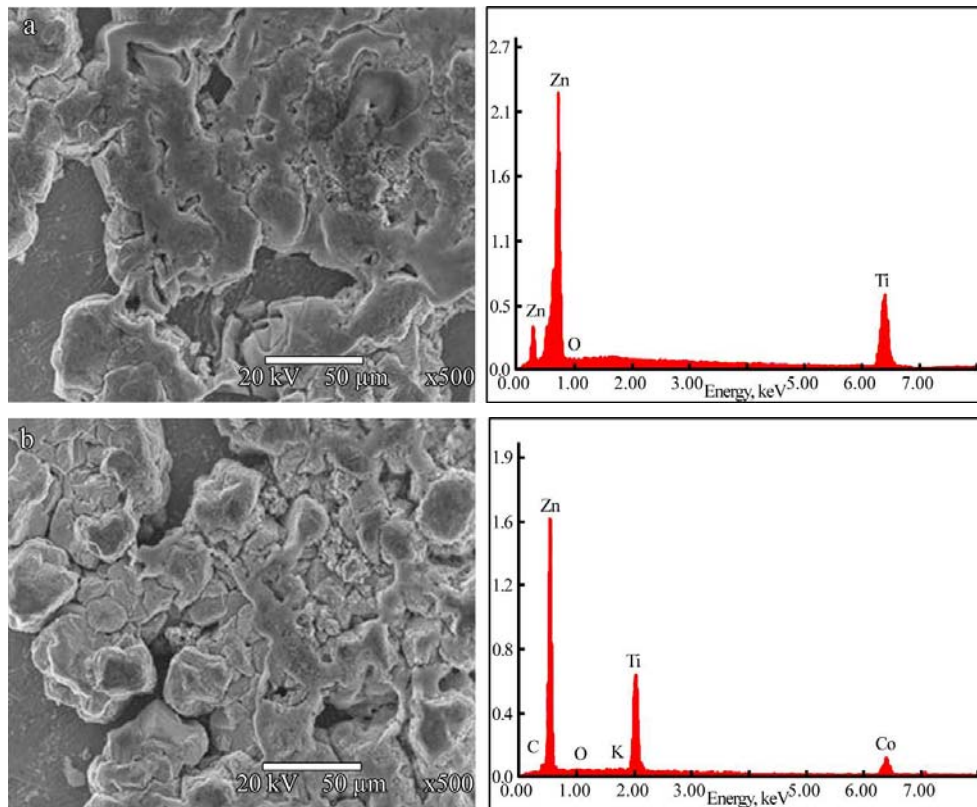
Element	C	Mn	Si	P	S	Al	Ni	Fe
Composition, %	0.15	0.45	0.18	0.01	0.031	0.005	0.008	Balance

**Table 2.** Bath composition of ternary Zn-Co-TiO<sub>2</sub> alloy co-deposition

Composition	Mass concentration (g/L)
ZnCl	100
KCl	50
Boric Acid	10
Glycine	10
TiO <sub>2</sub>	30
Cobalt Chloride	30
Parameter	Value
pH	4.8
Voltage	0.5–1.0 V
Time	20 min.
Temp	40°C

**Table 3.** Itinerary bath composition of ternary Zn-Co and Zn-Co-TiO<sub>2</sub> alloys co-deposition

Sample number	Sample material	Time of deposition (min)	Potential (V)	Current (A)
Blank (Control)	–	–	–	–
Sample 1	Zn-TiO <sub>2</sub>	15	1	2A
Sample 2	Zn-TiO <sub>2</sub>	15	0.5	2A
Sample 3	Zn-Co-TiO <sub>2</sub>	15	1	2A
Sample 4	Zn-Co-TiO <sub>2</sub>	15	0.5	2A

**Fig. 1.** SEM-EDS micrographs of: (a) Zn-TiO<sub>2</sub>, (b) Zn-Co-TiO<sub>2</sub> at 1.0 V.

possible to assume that the factors such as a lower potential and an effect of the surfactant additive, such as glycine and the metal ion arising from adsorbing metal ion, provide strong adsorption within the particulate and the cathode [32–35].

It is worth mentioning that the fabricated Zn-TiO<sub>2</sub> coatings have homogenous and non-porous appearances in some areas. Hence, the crystal-shape and a smaller growth occur as an expected result and are attributed to a strong blocking effect in the zinc

matrix, with EDS showing the admixed particulate being present.

Figure 1b with SEM – EDX images shows the ternary single bath Zn-Co-TiO<sub>2</sub> coated matrix. The grain size of the composite coated sample was smaller and more compactable when compared to that of pure Zn-TiO<sub>2</sub>. The dramatic improvement might be due to the presence of Co incorporation into the reinforced Zn-TiO<sub>2</sub> composite coatings. Though the presence of TiO<sub>2</sub> provides more nucleation sites and decelerates the crystal growth [16–19], < 1% Co has been reported in [23, 32–33] to greatly improve the structural behavior and retard deterioration four-fold. One strange characteristic of this ternary behavior of Zn-Co-TiO<sub>2</sub> was a uniform and continuous thickness, without many flaws. The obvious absence of this defect and flaws along the interface is significant for the present study and is an indication of a good coating matrix and good adhesion properties. In addition to the above, the optical micrographs display the overview of some coated samples as depicted in Fig. 2.

With titanium presence in zinc rich bath a noticeable change in the surface structure in milky-white spots are observed in Fig. 2a. The crystal dispatch at the interface seems to be more visible for all depositions at 0.5 V, as seen in Figs. 2a and c (compare to that of a higher voltage of 1.0 V in Figs. 2b and d). Thus, such occurrences are expected in some cases because researchers in [2–3] attest that lower plating potential tends to provide a better surface finish and strong adhesion.

In Figs. 2c and d, the grains of the deposit look smallest as affirmed in [23, 33], which is due to the suppressing action of Co in the admixed bath. At the background and interface, much more Co was found than TiO<sub>2</sub> particles (dark-grey spots on the optical micrograph). Trends to the absence of porosity and good homogeneous were found with all deposits, especially with lower magnification.

#### *XRD phase evaluation*

Surface changes of different coated samples with Co and TiO<sub>2</sub> was traced for the phase analysis. Figure 3 and 4 shows the XRD spectra corresponding to the used particulate coated samples at various phases. In Figure 3, compositions evolution of new phases, such as Zn<sub>2</sub>Ti<sub>2</sub>, ZnTi, Zn<sub>3</sub>Ti<sub>4</sub> and Zn<sub>2</sub>TiO, besides the original Zn-based particulate, was observed within the coated interface. Surprisingly, high strong peaks are due to the admixed particulate of Ti incorporated, resulting into co-deposition and, in turn, leading to the formation of a high-strength composite matrix.

The interaction between Zn and TiO<sub>2</sub> ultimately produces a crystal orientation of the grain size rather than chemical dissolution of Ti in the admixed for-

mation. Broadening phenomenon might as well been absorbed, and, as reported in [36], to have a heavier impact in the related binary, ternary and quaternary alloys because of the presence of nano-composites.

Moreover, the influence of Co and TiO<sub>2</sub> resulting into the structural grain refining and modification due to the real effect and precipitation of the crystallite size by the particle addition is displayed in Fig. 4. As mentioned above, the improvement of different crystal structures can be related to the surface energy differences, which become the driving force for the relative growth of grains owing to compactness.

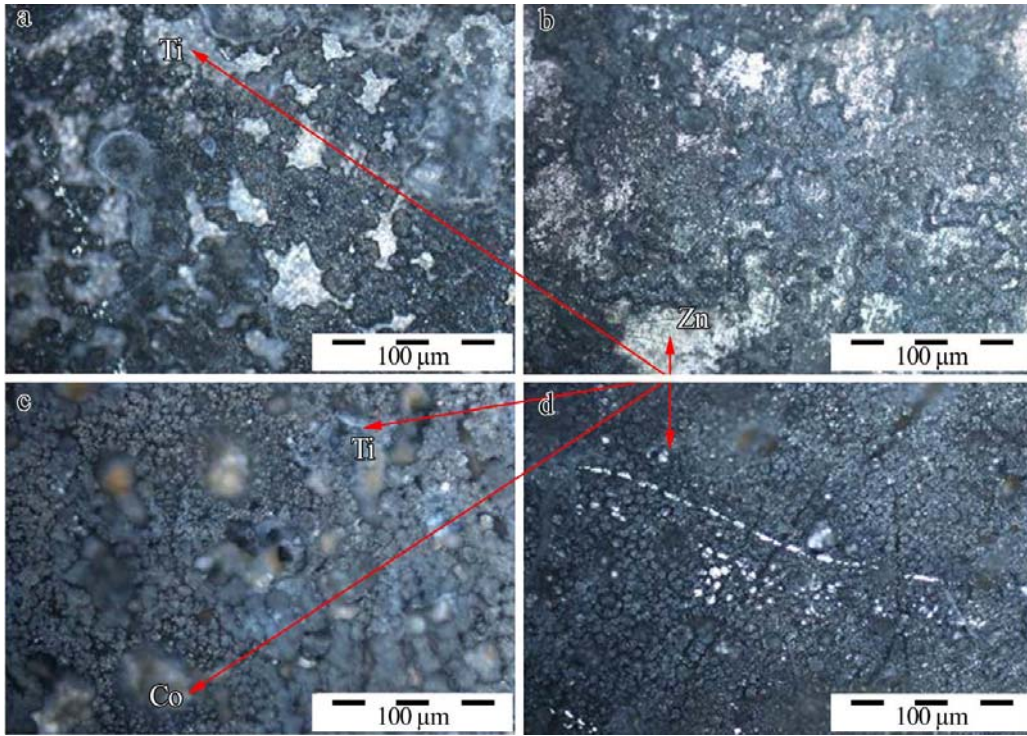
The presence of the intermediate dispatched composite phases observed with Zn-Co-TiO<sub>2</sub> series produced the highest peak with Zn<sub>2</sub>TiO and ZnOTiOCo in its lower multiphase. However this is expected and traceable to their inter-diffusion mechanism and ion of each particulate as described by [36]. In the other hand, vivid progressions of Zn hexagonal structure from all peak diffraction line were seen, which signifies harness performance and remarkable effect of the composite induced. Since, plane intensity is due to the modification of the metal surface by the adsorption of the molecules of the composite interacting with the zinc blend of different crystal planes, which will induce different growth structure.

Hence, good blend was found to exist within the matrix intensities of the admixtures. The significant participation of Co and Ti was mostly observed at higher intensities and the morphologies of the zinc matrix improved.

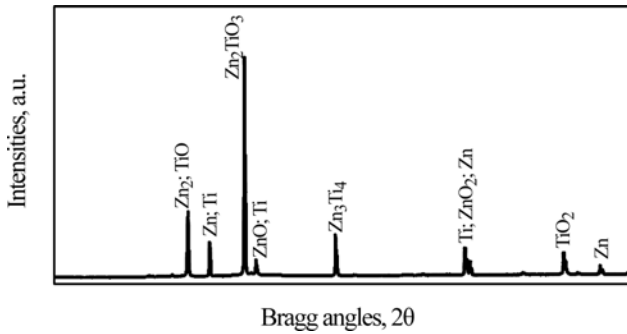
#### *Photo-electrochemical studies*

The linear potentiodynamic polarization test was carried out in 3.65% NaCl solution. The Tafel plots acquired for the coating are shown in Fig. 5. The anodic and cathodic Tafel constants and corrosion current density values derived after extrapolation are summarized in Table 4. The positive shift of  $E_{corr}$  to -1.2256 (mV) for Zn-Co-TiO<sub>2</sub> at 0.5 V indicates better corrosion resistance than that of Zn-Co-TiO<sub>2</sub> with -1.2625 (mV) coatings at 1.0 V, as shown in Fig. 4. The same trend also holds for the binary alloy system of Zn-TiO<sub>2</sub> with  $E_{corr}$  of -1.2637 mV at 0.5 V, which also provides a significant improvement against plating of the fabricated alloy at 1.0 V (1.3621 mV). In all cases, the potential of the formulated and fabricated coating matrixes yielded a better improved potential than of the as-received sample at -1.3773 mV. The corrosion rate and  $I_{corr}$  subsequently followed the same trend.

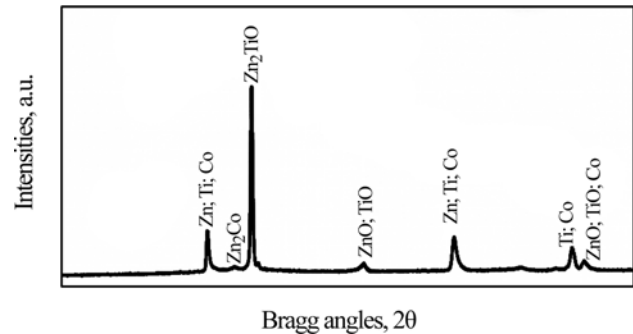
From Table 4 it can be also seen that the  $I_{corr}$  value of all coated mild steel samples is by five orders of magnitude lower than of the bare mild steel. For the TiO<sub>2</sub> admixed coated mild steel samples at



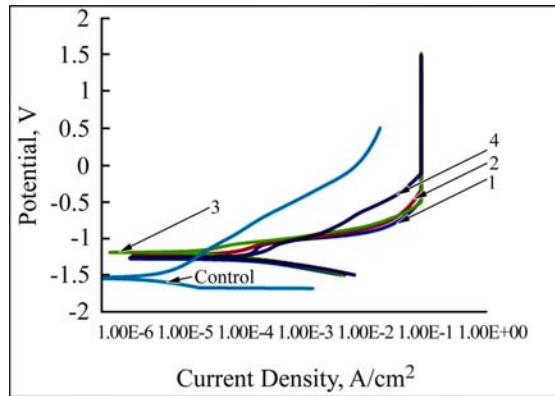
**Fig. 2.** Optical micrographs of: (a) Zn-TiO<sub>2</sub> at 0.5 V; (b) Zn-TiO<sub>2</sub> at 1.0 V; (c) Zn-Co-TiO<sub>2</sub> at 0.5 V; (d) Zn-Co-TiO<sub>2</sub> at 1.0 V all in 20 min.



**Fig. 3.** XRD spectra of Zn-TiO<sub>2</sub> at 1.0 V.



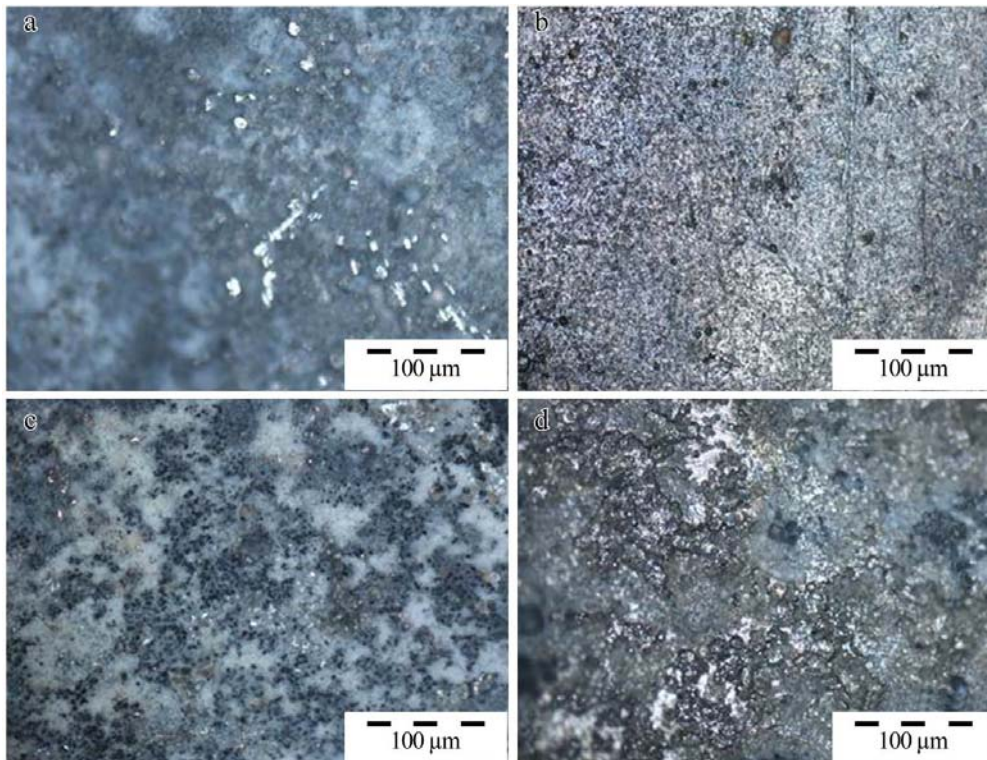
**Fig. 4.** XRD spectra of Zn-Co-TiO<sub>2</sub> at 1.0 V.



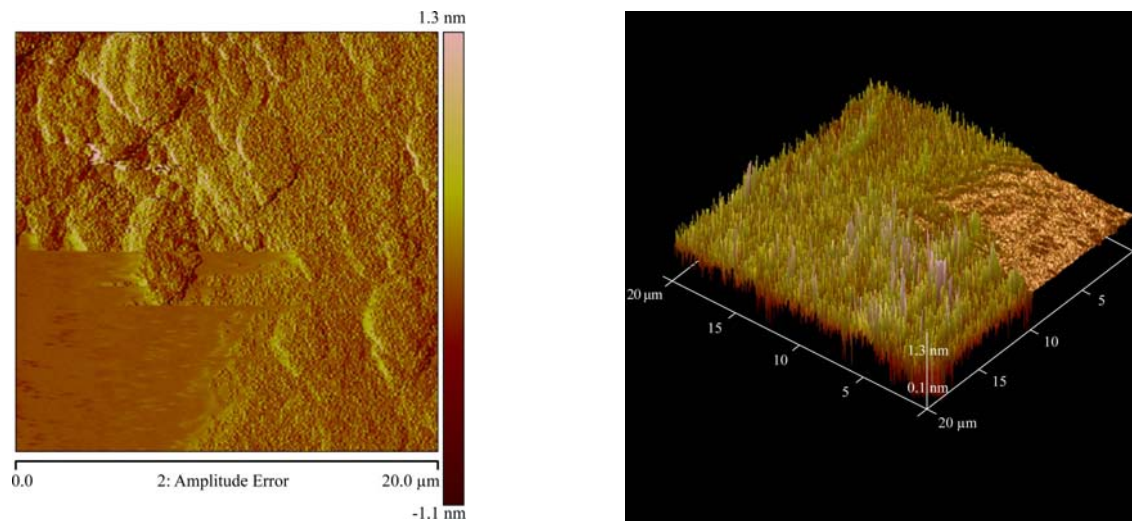
**Fig. 5.** Linear potentiodynamic polarization curves of coated and uncoated samples in 3.65% NaCl solution.

**Table 4.** Linear potentiodynamic polarization data of coated and uncoated samples in 3.65% NaCl solution

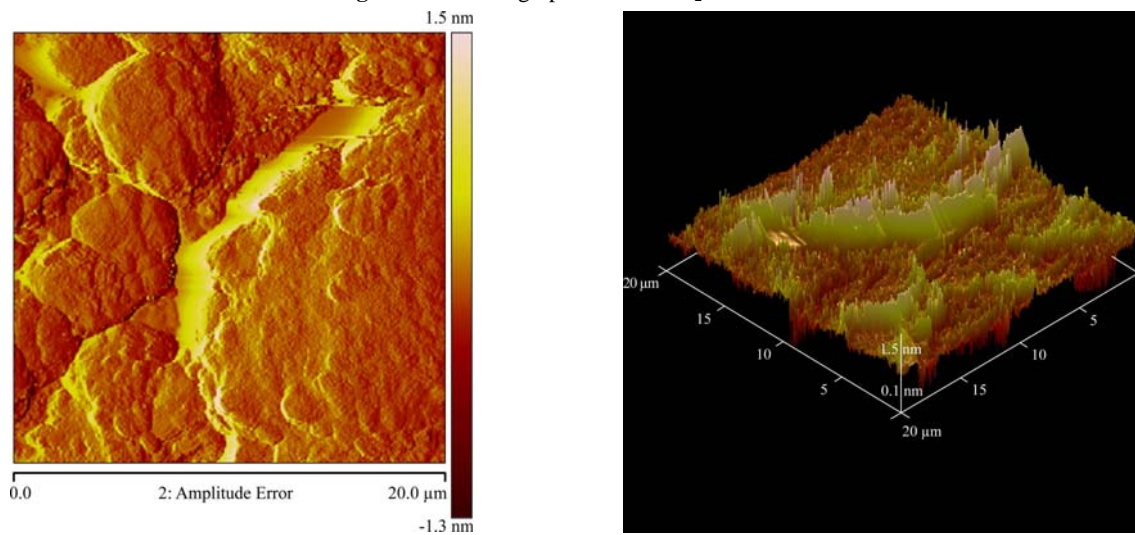
Sample	$E_{corr}$ , Obs (V)	$j_{corr}$ (A/cm <sup>2</sup> )	$i_{corr}$ (A)	CR (mm/y)	$R_p$ (Ω)	$E$ Begin (V)
Sample 1	-1.2637	6.53E-05	6.53E-05	0.35239	164.76	-1.2924
Sample 2	-1.3621	2.86E-05	2.86E-05	0.75826	136.91	-1.3022
Sample 3	-1.2256	2.11E-05	2.11E-05	0.24523	413.63	-1.2509
Sample 4	-1.2625	3.03E-05	3.03E-05	0.33264	222.96	-1.2851
Control	-1.5390	7.04E-02	2.04E-03	4.10000	27.600	-1.329



**Fig. 6.** OPM analysis of: (a) Zn-TiO<sub>2</sub> at 0.5 V; (b) Zn-TiO<sub>2</sub> at 1.0 V; (c) Zn-Co-TiO<sub>2</sub> at 0.5 V and (d) Zn-Co-TiO<sub>2</sub> at 1.0 V after corrosion.



**Fig. 7.** AFM micrographs of: Zn-TiO<sub>2</sub> at 0.5 V.



**Fig. 8.** AFM micrographs of Zn-Co-TiO<sub>2</sub> at 0.5 V.

all potentials,  $I_{corr}$  are by two orders of magnitudes lower than of the as-received sample. The beneficial effect of Co and  $TiO_2$  in the improvement of the corrosion resistance of this Zn-based coating may be due to a strong activity and affinity between Co,  $TiO_2$  and Zn, which is responsible for the development of a synergistic effect, while improving the corrosion resistance of the ternary coated mild steel.

So, the coatings improved the corrosion resistance of the mild steel substrate, adding to it a significant polarization resistance. This indicates that the admixed coating matrixes are promising as the substrate material but must be restrained to a certain potential of a coating to enforce compactness and cohesion.

Although the resistance behavior of materials certainly influences the corrosion rate [31–33], the polarization resistance of all of the coated samples was greatly improved in the following order: 3>4>1>2>Blank (control), with the  $R_p$  values of 413.63  $\Omega$ , 222.96  $\Omega$ , 164.76  $\Omega$ , 136.91  $\Omega$ , and 27.600  $\Omega$ , respectively. This tendency is attributed to the oxidation noticed on the surface of the modified coating. A more positive shift in the corrosion potential was found with Zn-Co- $TiO_2$ , having  $R_p$  of 413.63  $\Omega$ .

Figures 6a-d show the optical images of Zn- $TiO_2$  at 0.5 V, Zn- $TiO_2$  at 1.0 V, Zn-Co- $TiO_2$  at 0.5 V, and Zn-Co- $TiO_2$  at 1.0 V, after corrosion in the 3.65% NaCl solution. In general, all coated surfaces still look satisfactory even after corrosion examination. Those appreciable corrosion products were observed as white and darker spots. In the case of a composite coated samples, with Co admixed, the size of these products was minimal, with the homogenous corrosion occurrence. Generally, the  $TiO_2$  inclusion in the zinc deposit brings down the corrosion rate, thus reducing the metal loss.

The overall optical micrograph studies establish that the zinc-titanium coated surfaces have less corrosion products at the interface. The degree of the corrosion-caused deterioration was not visible at all for Zn-Co- $TiO_2$ . This indicates the effect of the Zn-Co- $TiO_2$  adhesion coated samples that have higher resistance to corrosion; those data were systematically compared to the results obtained by SEM studies.

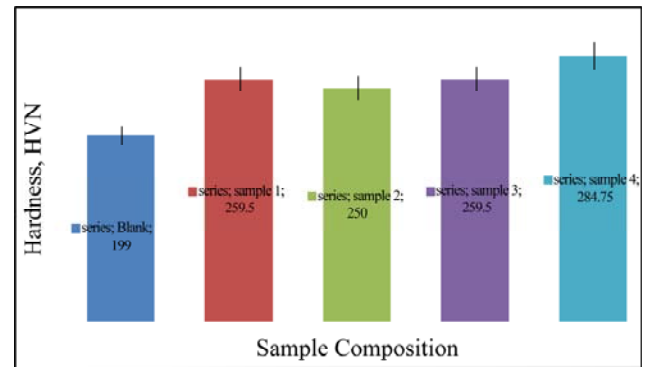
#### AFM analysis

The AFM was used to make an analysis of Zn- $TiO_2$  and Zn-Co- $TiO_2$ , both obtained at 0.5 V, as shown in Figs. 7 and 8. In both alloys deposited, a uniform crystallites coalesced with small grains were found affirming the morphological result obtained by SEM. The topography of Zn-Co- $TiO_2$  shows some undulation which expectedly might arise as a results of Co incorporation into the

Zn- $TiO_2$  matrix. The undulation progression within the interface by the additive might also necessitate the adhesion behavior of the coated alloys.

#### Microhardness studies

Figure 9 visualizes the effects of  $TiO_2$  and Co on the Zn interface at the applied voltage of 0.5 and 1.0 V. From all indicators, the microhardness rises with an additive dispersed into the bath. A pronounced microhardness change was noticed for samples 3 and 4 that contain the Zn-Co- $TiO_2$  matrix at their applied potential, suggesting the Co strengthening effect. Reports in [4, 5] tell us that ceramics composite particles can lead to refinement in the grain structure and improve the microhardness of the composite coatings. Thus the  $TiO_2$  composite changes cause smaller grains and provide structural modifications, which could enhance the hardness of the composite coatings [19, 27, 30]. Moreover, Co was attested to have compatibility properties in bath and its presence in the composite coatings improved their mechanical properties [23, 33].



**Fig. 9.** Variations of micro-hardness of: sample 1 – Zn- $TiO_2$  at 0.5 V; sample 2 – Zn- $TiO_2$  at 1.0 V; sample 3 – Zn-Co- $TiO_2$  at 0.5 V and sample 4 – Zn-Co- $TiO_2$  at 1.0 V, all in 20 min.

In line with the results, both Co and  $TiO_2$  particulate contribute immensely to the hardness behavior of the Zn- $TiO_2$  and Zn-Co- $TiO_2$  coatings; hence the absence of cracks and flaws, as earlier stated, is a prerequisite for the fabrication of a well adhered coating with good hardness properties. The coating alloys have a homogeneous composition, which shows there is no deleterious effect of the cracked morphology on the hardness properties. A significant difference could be seen from 199 Hv, in as-received samples, to 284 Hv, in as-observed ones, for sample 4 (Zn-Co- $TiO_2$ ) matrixes.

#### CONCLUSIONS

- In this work, mixed Co- $TiO_2$  films have been successfully deposited on mild steel substrates by electrolytic co-deposition. The alloy of Zn-Co- $TiO_2$  has been introduced to replace the Zn- $TiO_2$  and Zn-Co alloys in coatings.

- XRD results of the deposits have shown that the Zn-Co-TiO<sub>2</sub> alloy coatings consisted of Zn<sub>2</sub>Co, Zn<sub>2</sub>Ti, ZnTiCo and ZnCo<sub>13</sub> phases.

- The Zn-Co-TiO<sub>2</sub> coatings showed better adhesion strength compared to that of Zn-TiO<sub>2</sub> alloy coatings.

- In general, from the morphological, mechanical and electrochemical studies, Zn-Co-TiO<sub>2</sub> alloy coatings have shown better performance than Zn-TiO<sub>2</sub>, in terms of displaying a trend for homogeneous diffusion and good interfacial properties. With the presence of Co, a wide application can be the base for commercialization.

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### Реферат

Исследовано получение композита из частиц цинк-кобальт и оксида титана методом электроосаждения с однорастворным электролитом. Были получены цинковые покрытия, модифицированные кобальтом, с включением оксида титана при оптимизированных параметрах процесса. Морфологические и микроструктурные характеристики были определены с помощью рентгеновского дифрактометра и сканирующего электронного микроскопа, оснащенного энергодисперсионным спектрометром. Механические характеристики покрытий определялись с применением микротвердомера Dura Scan. Коррозионные свойства оценивались методом линейной потенциодинамической поляризации с применением потенциостата VA 669 PG STAT 101. Было выявлено, что композитное покрытие цинк-кобальт с включением субмикронных частиц TiO<sub>2</sub> обладает хорошими характеристиками. Установлено наличие улучшенных характеристик межфазного взаимодействия между основой и композитом. Оценка структуры осажденных покрытий с помощью сканирующего электронного микроскопа, оптической и атомной силовой микроскопии показала формирование однородной зернистой структуры. При изменении параметров процесса и содержания кобальта и частиц TiO<sub>2</sub> существенно повышается коррозионная устойчивость и улучшаются микромеханические характеристики покрытий.

*Ключевые слова:* межфазная граница, коррозия, упрочнение, структурные характеристики.