

Surface modification, strengthening effect and electrochemical comparative study of Zn-Al₂O₃-CeO₃ and Zn-TiO₂-CeO₃ coating on mild steel

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Abstract Surface enhancement of engineering materials is necessary for preventing service failure and corrosion attacks industrially. The surface modification, strengthening effect and electrochemical comparative study of Zn-Al₂O₃-CeO₃ and Zn-TiO₂-CeO₃ coating on mild steel was investigated. Deposition was performed to obtain a better surface adherent coating using the electrodeposition technique. Co-deposition of mild steel resulted into surface modification attributes to the complex alloys that were developed. Films of mild steel were electrodeposited on zinc electrodes using the chloride bath solutions. The effect of deposition potentials was systematically studied using a focus ion beam scanning electron microscope (FIB-SEM) and an atomic force microscope (AFM) to observe the surface morphology, topography and the surface adherent properties of the coatings. The elemental composition and the phases evolved in composite

coatings were measured by means of the energy dispersed spectrometer (EDS). The microhardness measurements and corrosion behaviours of the deposits were investigated. Weight loss measurement was conducted on the plated samples to observe the rate of corrosion and it was observed that there was severe corrosion on the controlled sample in comparison to the plated samples and that Zn-TiO₂-CeO₃ resisted more corrosion attacks.

Keywords Electrodeposition · Microstructure · Corrosion and hardness

1 Introduction

Electrodeposition provides a convenient means of applying a protective coating of one metal on another. A particular attraction is the ability to control the thickness and uniformity of the coatings fairly accurately through the Faradaic equivalent of the total electric charge passed, allowing for any inefficiencies [1, 2]. This permits the surface qualities of expensive metals such as zinc, nickel and tin to be imparted to metals of lower value, such as steels, by applying them as very thin coatings [3, 4]. Often, a coating is required to have both a protective value and an aesthetic appeal and in that case there is a further economy in using electrodeposition because it is usually possible to produce bright decorative finishes that require no subsequent treatment [5].

Zinc coatings are used extensively to protect steel. They are well suited for the purpose because zinc is inexpensive, the coating process is easy and the protection is galvanic and very effective [6, 7]. Electrodeposition is used as an alternative to hot-dip galvanising where the higher cost is justified by close dimensional tolerances, as in screw threads or by improved appearance. Bright deposits are technically feasible but the

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cost is not often justified for the utilitarian applications for which zinc coatings are used [8].

Zinc coatings are obtained either from cyanide, non-cyanide alkaline or acid solutions. Because of the pollution and high cost associated with cyanide, deposition from other baths such as sulphate, chloride, and mixed sulphate-chloride baths are gaining importance [9, 10]. Good deposition depends mainly on the nature of bath constituents. Generally, a plating bath contains conducting salts, complexing agents and metal ions. Among these the complexing agents influence the deposition process, solution properties and structure of the deposit. The action of these complexing agents depends on pH, nature of anion, temperature and other ingredients of the medium [11, 12]. One of the ways to improve the corrosion resistance of zinc coatings consists of alloying zinc with group eight metals (Fe, Co, Ni) [11]. Thus, Zn-Ni alloys provide a superior sacrificial protection to steel than pure zinc since they corrode more slowly, and are successfully used especially in the automobile and aeronautical industry [12]. An alternate way for further enhancing the corrosion resistance of zinc coatings on steel consists in generating composite coatings on its surface by electrolysis of plating solutions, in which micron or sub-micron sized particles (i.e. TiO₂, SiO₂, Al₂O₃ etc.) are used [13, 14].

Among the oxides used for enhancing the corrosion resistance of the coatings, Al₂O₃, CeO₂ and TiO₂ are particularly interesting, due to their resistance to high temperature oxidation, corrosion, mechanical abrasion and wear [13, 14]. Li et al. [15] reported on the development of nanocomposite coatings consisting of TiO₂ in the form of anatase and rutile in the Ni matrix via electrochemical deposition technique, Aruna et al [16] showed an enhanced performance of wear and corrosion characteristics of Ni-based composite coatings by embedding with alumina yttria-doped cubic zirconia (AZY, (1-x) Al₂O₃-8 mol % yttria stabilised xZrO₂ (x=10 wt%)) particles. Work by Erler et al [17] on Ni-Al₂O₃ composite coatings reported poor corrosion resistance compared to the monolithic Ni. Szczygieł and Kołodziej [18] reported that the lower corrosion resistance of Ni-Al₂O₃ could be due to the poor bonding between the oxide particles and the matrix, which can increase the possibility of dissolution of loosely held Al₂O₃ (alumina) particles at high potentials and result in more nickel exposure to the electrolyte for corrosion attack. Aruna et al. [19] reported on the corrosion properties of Al₂O₃-embedded Ni composites that showed the oxide

Table 1 Chemical composition of mild steel used during the investigation (wt%)

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 Summarised data for the deposited samples using Zn-Al₂O₃-CeO₃/Zn-TiO₂-CeO₃ chloride bath

Composition	Mass concentration (g/L)
Zn	80
KCl	40
Boric acid	10
Glycine	10
Al ₂ O ₃	7.5–12.5
TiO ₂	7.5–12.5
CeO ₃	7.5–12.5
Ph	4.8
Current	1.5–2.0 A
Time	10 min
Temperature	40 °C

phase-dependent corrosion performance. Their studies indicated that the corrosion resistance of Ni-αAl₂O₃ was better than the corrosion resistance of Ni-γAl₂O₃ as well as the Ni-α and γAl₂O₃ mixtures; however, the reason for such behavior was not explained.

CeO₂ incorporated in zinc was reported as a corrosion inhibitor [20], due to the fact that cerium oxides and hydroxides hinder the cathodic reduction reaction. Moreover, Ce⁴⁺ ions are able to promote the superficial oxidation of metals, conferring a natural protection layer because of their high oxidation potential. Ceria layers electrodeposited from cerium nitrate solutions in the presence of PEG on zinc-electroplated steel or cerium-based oxides films were elaborated by cathodic electrodeposition from relatively concentrated cerium nitrate solutions on carbon steel [21]. On the other hand, CeO₂ nanoparticles embedded in hot dip zinc coatings [22] caused a significant improvement in galvanic and other physical characteristics of the coatings. It was reported that nanosized TiO₂ electrocodeposited with zinc confer an enhanced resistance against corrosion and better mechanical properties to the corresponding zinc coatings [23]. Despite the number of papers reporting the beneficial effects of Al₂O₃, CeO₂ and TiO₂ on the corrosion resistance of Zn coatings, to the best of our knowledge, there are no reports on the combined effect of these oxides on zinc-electroplated steel or on the use of ternary Al₂O₃, CeO₂ and TiO₂ oxides. Moreover, it should be mentioned that the electrolytic co-deposition of inert particles and metals is a very complex process. Although several experimental and theoretical studies on the particle co-deposition mechanism have been published, the process is not yet well understood. In this context, the present work reports the results obtained for the preparation of composite Zn coatings on steel by using ternary Al₂O₃, TiO₂ and CeO₂ oxides. In an attempt to correlate the effects of the particles with their characteristics and with the properties of the composite deposits, the anti-corrosion properties of Zn-TiO₂-CeO₂ layers are compared with those of Zn-Al₂O₃-CeO₂ composites coating.

2 Materials and method

2.1 Materials

A flat plate of mild steel (20 mm×20 mm) substrate was used in this research. The composition of the steel is shown in Table 1. Other materials employed for the purpose of this work include pure zinc plate anode, pure titanium oxide and aluminium oxide powder and pure zinc powder.

2.2 Method

2.2.1 Composition and fabrication of coating

The mild steel samples were dipped into 1 M of HCl solution for 5 s followed by rinsing into the de-ionised water. Analytical grade chemicals and de-ionised water were used to prepare the plating solutions at 40 °C, to easily dissociate any agglomerate in the bath. During the plating, the solution was stirred using the magnetic stirrer for the solution to plate well on the mild steel. The bath compositions admixed for the coatings are shown in Table 2 and they were prepared 2 weeks in advance for the plating to proceed successfully and plate better with increased time.

2.2.2 Preparation of the coatings

The prepared Zn-Al₂O₃-CeO₃/Zn-TiO₂-CeO₃ composites were heated for 10 min and systematically agitated to obtain a homogeneous solution before the electrolytic deposition process in an electrolytic cell, whereby the prepared cathodes and anode were connected to the direct current power supply through a rectifier at a controlled current of 1.5A/cm² and 2.0A for 10 min with the varying voltage. The distance between the anode and the cathode with respect to the immersion depth was kept constant; lastly the samples were rinsed in distilled water and dried. The table of formulated bath compositions of Zn-Al₂O₃-CeO₃/Zn-TiO₂-CeO₃ is shown in Table 3.

Table 3 Itinerary bath compositions of ternary Zn-Al₂O₃-CeO₃/Zn-TiO₂-CeO₃ alloy Co-deposition

Sample order	Material sample	Time of deposition (min)	Current density (A/cm ²)
Blank	-	-	-
Sample 1	Zn-Al ₂ O ₃ -CeO ₂	10	1.5
Sample 2	Zn-Al ₂ O ₃ -CeO ₃	10	2.0
Sample 3	Zn-TiO ₂ -CeO ₃	10	1.5
Sample 4	Zn-TiO ₂ -CeO ₃	10	2.0
Sample 5	Zn-Al ₂ O ₃ -TiO ₂ -CeO ₃	10	1.5
Sample 6	Zn-Al ₂ O ₃ -TiO ₂ -CeO ₃	10	2.0

2.2.3 Characterisation of the electrodeposited samples

The surface appearance and morphology of the coating and thin films were characterised using a JSM-5800LV scanning electron microscope with the energy dispersive x-ray analyser (SEM/EDS) at 50 µm using the magnification of 500. The adhesion profile, topography and morphology of the sample surface before and after coating were observed with the aid of atomic force microscope (AFM).

The Emco-test microhardness tester machine works on the basic premise of measuring the critical dimensions of an indentation left by a specifically dimensioned and loaded indenter and is a modern hardness equipment that automatically evaluates the hardness value on the screen. Indentations of five points for 15 s dwell with 100 g of load were placed on the surface of each specimen to accurately measure the errors and the average was calculated.

2.2.4 Weight loss corrosion test

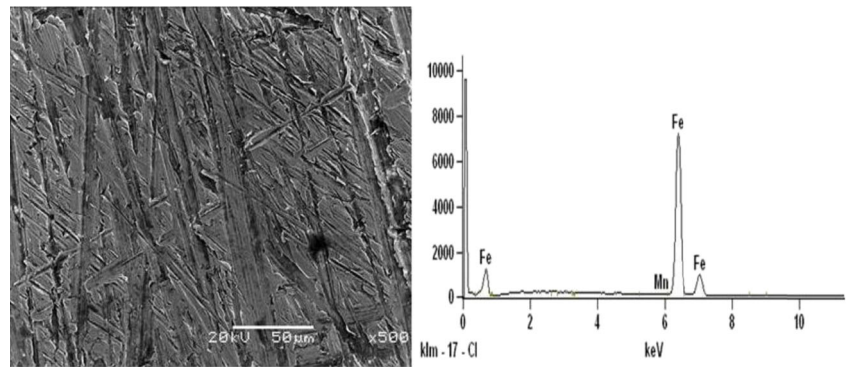
The deposited mild steel samples were immersed in a seawater environment for a period of 14 days, along with the unplated sample as control. The electrode potential measurements between the sample surface and the chloride environment were done at a regular interval of 48 h. The samples were taken out of their respective 250 ml glass beakers using a spatula and a paper towel to wipe the sample dry before being weighed on a Lasec Analytical balance for the masses to be recorded, and the beakers were then covered with the parafilm to avoid contact with the environment. The corrosion rates in g/cm²/year were obtained from the weight loss analysis using the expression [13]: $C_R = KW/(DAT)$ cm²/year.

Where D is the weight loss in mg, A is the total surface area of the specimen in cm², T is the exposure time in days extrapolated to a year, W is the corrosion penetration rate expressed in area per year and K is the constant 87.6.

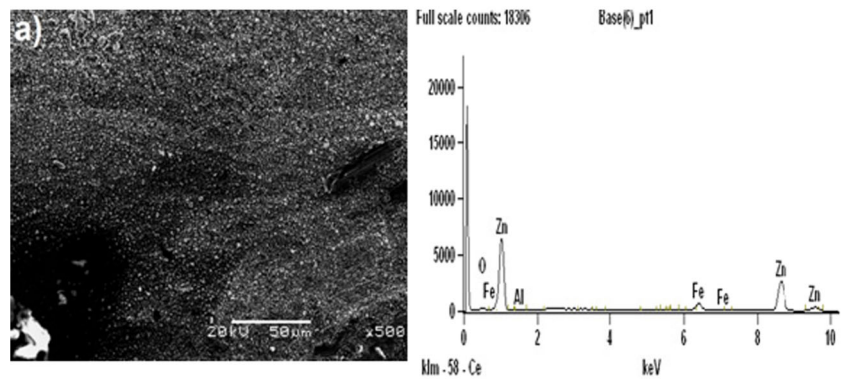
3 Results and discussion

Figure 1a, shows the SEM/EDS micrograph of the mild steel substrate of the as-received, which was used for the formation

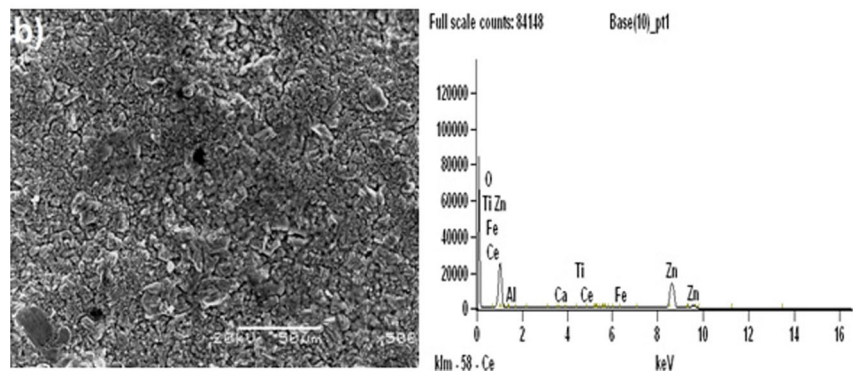
Fig. 1 **a** SEM/EDS micrograph of the as-received mild steel sample, **b** SEM/EDS micrographs of [a] Zn-7.5 Al₂O₃-7.5 CeO₃ 10 min at 1.5 A, ×1000, **c** SEM/EDS micrographs of [b] Zn-7.5 TiO₂-7.5 CeO₃ 10 min at 1.5 A, ×1000, and **d** Zn-7.5 Al₂O₃-7.5 TiO₂-7.5CeO₃ 10 min at 1.5 A, ×1000 magnification



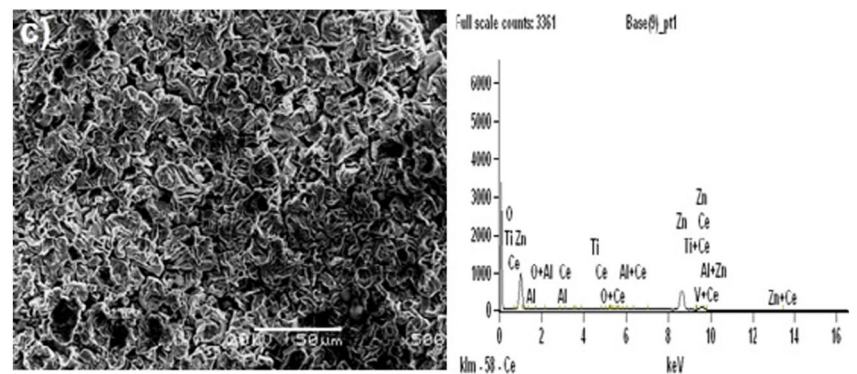
a: SEM/EDS micrograph of the As-received mild steel sample



b: SEM/EDS micrographs of [a] Zn-7.5 Al₂O₃-7.5 CeO₃ 10min at 1.5A, X1000



c: SEM/EDS micrographs of [b] Zn-7.5 TiO₂ -7.5 CeO₃ 10min at 1.5A, X1000



d: Zn-7.5 Al₂O₃-7.5 TiO₂-7.5CeO₃ 10min at 1.5A at 1000x magnification.

and co-deposition of the mild steel. The Fig. 1b–d displays the SEM/EDS micrographs of [b] Zn-7.5 Al₂O₃-7.5 CeO₃ 10 min at 1.5 A, [c] Zn-7.5 TiO₂-7.5 CeO₃ 10 min at 1.5 A and [d] Zn-7.5 Al₂O₃-7.5 TiO₂-CeO₃ 10 min at 1.5 A, respectively. From the general observation of the SEM/EDS images it can be seen that the thin film formed on the mild steel samples resulted into good appearance, better plating and good adhesions than the substrate (control).

According to Naik et al., [4] the nature of the surface morphology and the orientation in the Fig. 1b–d image reveals, homogeneous appearance with very small grains formed. These may be attributed to the possibility that the deposition behaviour and the adhesion strength of any particular plating is often based on the potential, current density, composition and the time of deposition. But, in this present study, the current density and the particles have a great effect on the morphology. It can be observed that Fig. 1b displays the aluminium with a minimal matrix to show that there is a better morphology due to the composite infiltration of the zinc bath causing an adherence and uniform deposit. In addition, it is expected that agglomeration will be observed within the zinc matrix which displays a high peak, but it was assumed that factors such as less potential, the effect of surfactant additives and the metal arising from absorbing metal ion provide a strong adsorption. This is in par with the work of Meenu et al. [14].

Figure 1c, shows the surface morphology of Zn-TiO₂-CeO₃ co-deposits, from the images, it was observed that the incorporation of the TiO₂ along with the boric acid and glycine in the electrolyte influences the morphological behaviour and resulted in fine grains with uniform blend with a smooth-like surface. From the Fig. 1c, the presence of elements of Ti and Ce were clearly shown in the EDS spectrum.

Figure 1d displays all the elements that were present in the solution from the SEM/EDS with addition to some trace elements that were not possible to be present. The SEM image displays a large grain size to show that there was crystal growth in the metal, which resulted in less porous spaces between the particles. The traces of CeO₃, TiO₂ and Al₂O₃ were less detectable due to the amount of the composition that was used in the bath solution. The grain size of Fig. 1d displays larger grain sizes in comparison to the other SEM images.

Analysis using AFM was performed on Zn-Al₂O₃-CeO₃, Zn-TiO₂-CeO₃ and Zn-Al₂O₃-TiO₂-CeO₃ as shown in Fig. 2 to support the SEM analysis. From Fig. 2, it was clearly shown that the uniformity of the coating was achieved. Fig. 2a,b displays on fine grain size when compared with Fig. 2c with large grains and good surface deposition. From both the SEM and AFM observation, one can infer that the TiO₂ in the bath displays a better surface adhesion.

Figure 3, showed the coating per unit area obtained for the various compositions under investigation. From Fig. 3, it is clearly shown that the coating obtained depends on the composition of the oxide and that of the additive. As the additive

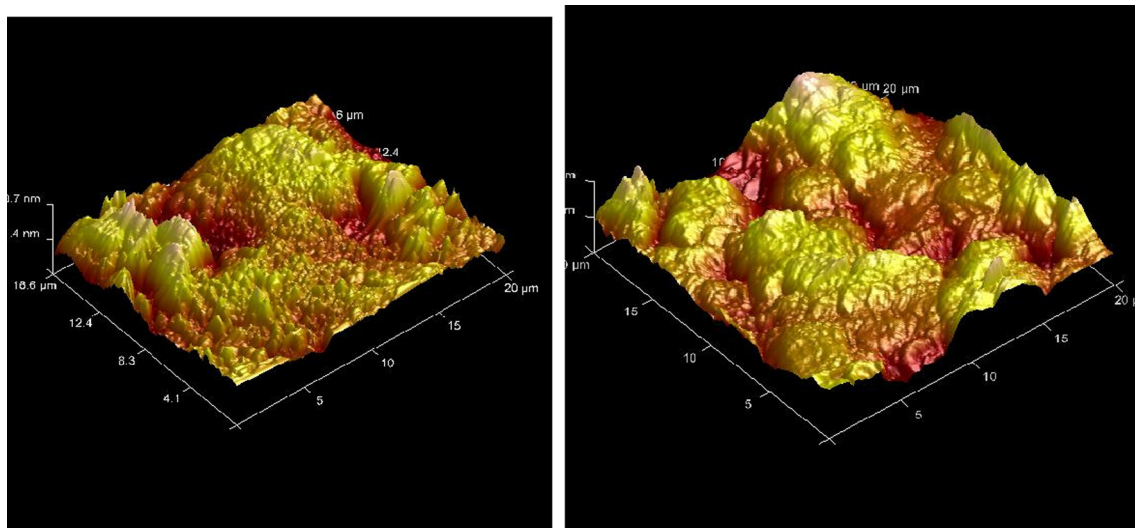
concentration is increased from 7.5 to 12.5 g, the coating per unit area also increases. Also the Zn-TiO₂-CeO₃ has the higher coating per unit area among all of them because of the more fine smaller grain size.

The hardness of plated metals depends on many factors and the most important is the plating bath composition and current density. Fig. 4, shows mild steel in different bath solutions at an applied current of 0.5 and 2.0 A at 10 mins on the zinc interface. TiO₂ displays a greater hardness value at 0.5 A than all the other components. According to Berner et al [8], the higher hardness of the coating was due to the fine-grained structure of the deposit and the dispersed particles in the fine-grained matrix may obstruct the easy movement of dislocations which was shown by the higher hardness value of the composite coated samples. As seen in Fig. 1, the deposit becomes finer-grained in the presence of TiO₂ and Al₂O₃ due to the fact that the particles interfere with the nucleation-growth process. Thus, the particles enhance nucleation by creating disorder in the incorporation of atoms into the lattice or inhibit surface diffusion of atoms towards growing centers and exert a detrimental effect on the crystal growth. This effect of grain refining is beneficial for the hardness values of the deposits.

The presence of particles in the metallic deposit may cause a change in the crystalline structure of the metal layer. Thus, it shows that crystal size decreases in the presence of TiO₂ particles in the bath deposit. The same investigations were performed in the case of Zn-CeO₃ deposits prepared in the presence of Al₂O₃ particles. The decrease in crystal size could be explained through the dynamics between the two processes: nucleation and crystal growth in the presence of particles. The smallest crystal size was obtained at the addition of TiO₂, hence it has higher hardness values than the Al₂O₃, or Al₂O₃/TiO₂ bath. For the same current regime, the addition of Al₂O₃ or TiO₂ in the zinc-CeO₃ deposit increased its microhardness, but it was because of the decrease of the grain size and the increase of deposit compactness. The microhardness values were slightly higher when TiO₂ was used.

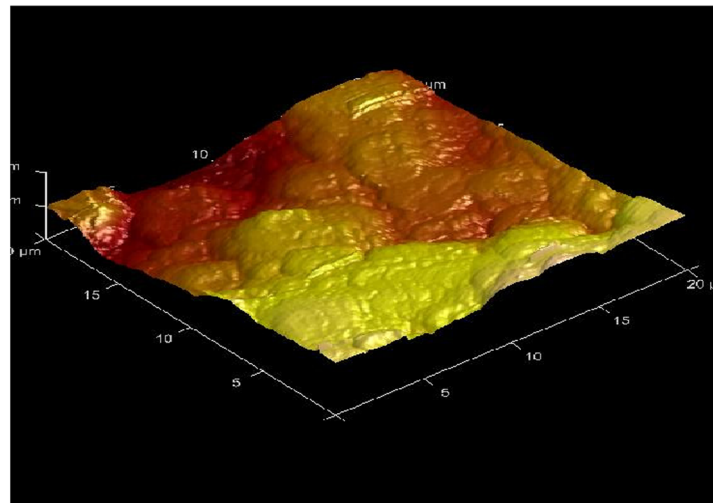
The results of the corrosion rate and electrodeposition efficiency obtained for the weight-loss method are showed in Fig. 5a–d. From Fig. 5a–d, it was observed that increase in time results in the increases of the corrosion rate of the samples either as a control or plated sample. The Zn-TiO₂-CeO₃ sample has the lesser corrosion rate as the exposure time increased. It was observed that the presence of TiO₂ with zinc resulted in the sample being the one with a higher corrosion resistance. Time of exposure plays a vital role in the corrosion of the samples and it was obtained that at a lower time of 48 min, the samples coated with Zn-TiO₂-2 have a 100% protection efficiency.

One can notice that the presence of TiO₂ and Al₂O₃ may shift the corrosion potential towards more positive values and decreases in the corrosion rate. As expected, as we can see in Fig. 5a–b, the Zn-TiO₂-CeO₂ and Zn-Al₂O₃-CeO₂ may have a positive potential than those observed in the same conditions



a: Zn-7.5 Al₂O₃-7.5 CeO₃ 10min at 1.5A,

b: Zn-7.5 TiO₂-7.5 CeO₃ 10min at 1.5A,



c: AFM micrographs of Zn-7.5 Al₂O₃-7.5 TiO₂-7.5 CeO₃ 10min at 1.5A.

Fig. 2 a Zn-7.5 Al₂O₃-7.5 CeO₃ 10 min at 1.5 A, b Zn-7.5 TiO₂-7.5 CeO₃ 10 min at 1.5 A, c AFM micrographs of Zn-7.5 Al₂O₃-7.5 TiO₂-7.5 CeO₃ 10 min at 1.5 A

for pure Zn coatings [2, 9], suggesting a more noble character of the deposit, which could be associated to an inhibition of the anodic reaction and, consequently, to a higher corrosion resistance. The decrease of the corrosion rate of the Zn-TiO₂-CeO₃ and Zn- Al₂O₃-CeO₂ coating could be due either to grain refinement of the deposit. The decrease in crystal size could be explained through the dynamics between the two processes: nucleation and crystal growth in the presence of TiO₂ and Al₂O₃ particles or to the fact that the incorporation of inert TiO₂ and Al₂O₃ in the coatings isolates them from the corrosion medium and distracts the corrosion current.

From the results of the corrosion rate at varying currents (see Fig. 5a–d), it was observed that the corrosion rate of the samples decreased after coating and that the rate of corrosion depended on the bath composition, time of exposure and

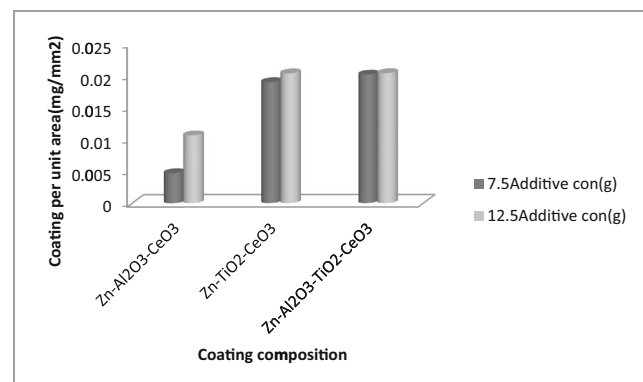
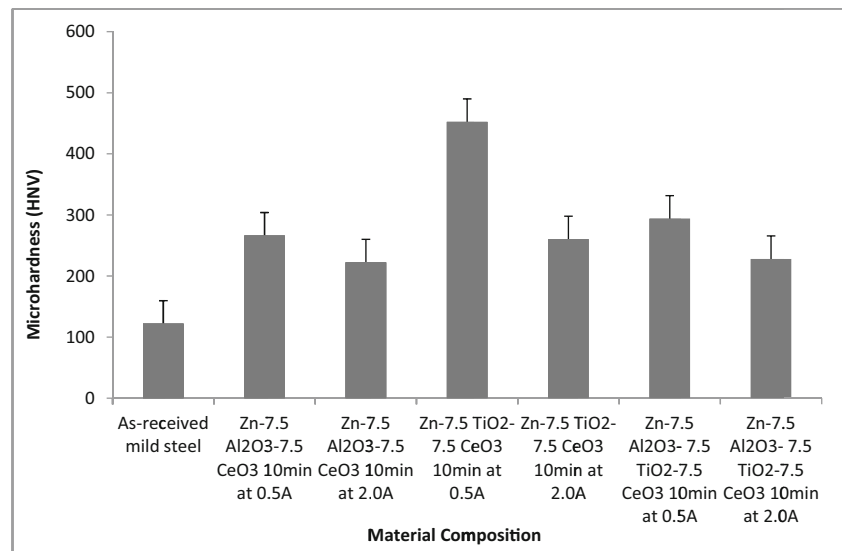


Fig. 3 Variation of coating per unit area with coating composition

Fig. 4 Variation of micrographs of [a] as-received mild steel, [b] Zn-7.5 Al₂O₃-7.5 CeO₃ 10 min at 0.5 A, [c] Zn-7.5 Al₂O₃-7.5 CeO₃ 10 min at 2.0 A, [d] Zn-7.5 TiO₂-7.5 CeO₃ 10 min at 0.5 A, [e] Zn-7.5 TiO₂-7.5 CeO₃ 10 min at 2.0 A, [f] Zn-7.5 Al₂O₃-7.5 TiO₂-7.5 CeO₃ 10 min at 0.5 A, and [g] Zn-7.5 Al₂O₃-7.5 TiO₂-7.5 CeO₃ 10 min at 2.0 A



current of plating. It was clear that as the time of exposure increased, the corrosion rate of the samples rises. This may be attributed to the fact that the corrosion product form with time was not able to serve as a protecting film for the steel. As the current of plating decreased from 2 to 1.5 A, the corrosion resistance of the samples improved. Zn-TiO₂-CeO₃ has a lesser corrosion rate as compared to the other samples, this shows that TiO₂ displays a better corrosion resistance as compared to Al₂O₃ even when the current is increased to plating is increased to 2.0 A. The TiO₂ oxide layer with a fine grain size can easily release the thermal stress and therefore prevent crack propagation.

According to Sadiku-Agboola et al. [11], the presence of TiO₂ in the coating significantly decreases the dissolution of Zinc on the mild steel surface. Also, TiO₂ form a strong passive film that prevents the metal from higher corrosion loss. The excellent corrosion resistance of TiO₂ results from the formation of a very chemically stable, highly adherent, and continuous protective oxide film on the surface. Because titanium itself is highly reactive and has an affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly in the metal surfaces. Improved corrosion resistance of TiO₂ composites was also attributed to the inhabitant behavior of TiO₂ particles at the grain boundaries and triple junctions, which are the usual sites for corrosion attack. With a decrease in current density of the bath, a decrease in the corrosion rates was also demonstrated because of the increased number of inhabited sites, which reduce penetration of the corrosive solution into the composite coatings.

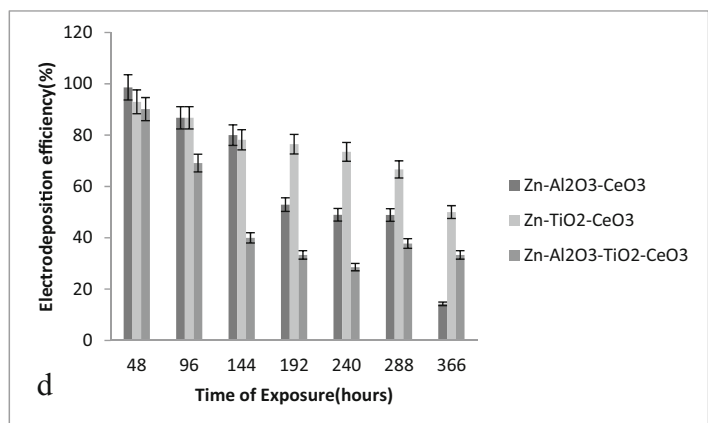
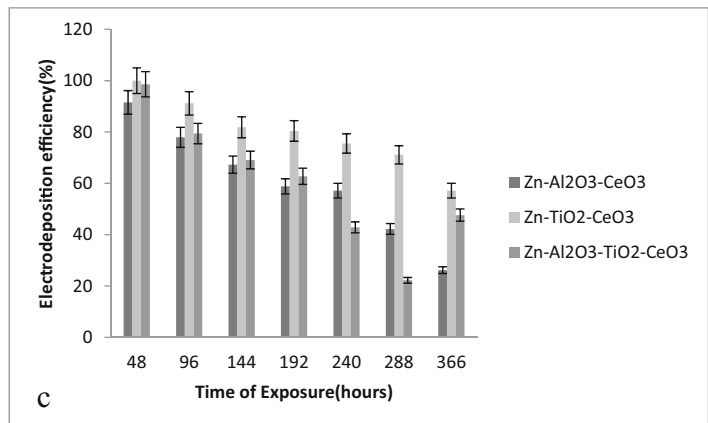
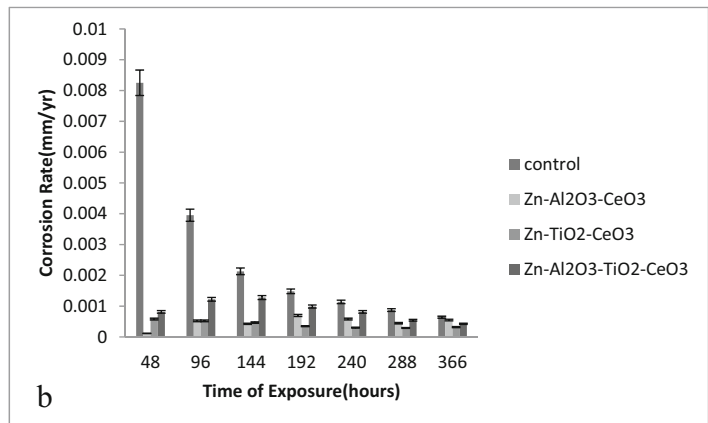
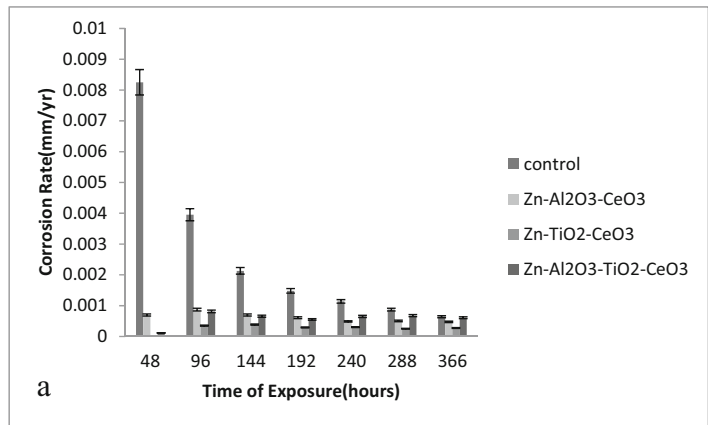
TiO₂ particles confer to Zn-CeO₃ deposits a greater corrosion protection than Al₂O₃ particles, influencing the corrosion process in terms of its bracking; current density of the

deposition affects the corrosion resistance of the resulting composite layers. Under the examined conditions, the existence of an optimal current density was pointed out, which was proven to be at 1.5 A/cm². The existence of an optimal current density in the plating bath is the result of the existence of two contrary effects which are the consequence of their incorporation in the metallic matrix: a beneficial one (the embedded inert oxide particles diminish the active surface in contact with the corrosive environment) and a detrimental one (in higher concentrations, they disturb the electrocrystallization process which may enhance corrosion).

It should be mentioned that the decrease of corrosion values is more significant also only for Zn-CrO₃-TiO₂ obtained from solutions of current density of 1.5 A/cm² proving that for this current density, the particles incorporated in metal deposits have an inhibiting effect on metal corrosion. This effect could be due to a more uniform incorporation of the particles in the metallic deposit leading to a decrease of the active surface in contact with the corrosive environment. On the other hand, TiO₂ particles have a low level of electronic conductivity and when they are uniformly dispersed in the composite coating, they can distract the corrosion current.

Comparing the corrosion rate values for Zn or Zn-CeO₃ deposition as reported [2, 9] from previous work with Zn-CrO₃-TiO₂ and Zn-CrO₃-Al₂O₃, it was observed that the highest value of corrosion resistance of Zn-CrO₃-TiO₂ and Zn-CrO₃-Al₂O₃ should provide the best protection. The values of corrosion rates of Zn-CrO₃-TiO₂ and Zn-CrO₃-Al₂O₃ calculated for composite coatings differ from those corresponding to pure Zn or Zn-CeO₃ deposits, indicating that the embedded Al₂O₃ or TiO₂ particles influence the kinetics of both anodic and cathodic processes.

Fig. 5 **a** Variation of corrosion rate with time of exposure for electrodeposited mild steel at 1.5 A for 10 min for a period of 336 h, **b** Variation of corrosion rate with time of exposure for electrodeposited mild steel at 2.0 A for 10 min for a period of 336 h, **c** Variation of electrodeposition efficiency with time of exposure for electrodeposited mild steel at 1.5 A for 10 min for a period of 336 h, **d** Variation of electrodeposition efficiency with time of exposure for electrodeposited mild steel at 2.0 A for 10 min for a period of 336 h



4 Conclusions

From the results and discussion mentioned previously, the following conclusions can be made:

1. Electrodeposition of Zn-Al₂O₃-CeO₃/Zn-TiO₂-CeO₃ was successfully carried out onto the surface of mild steel substrates.
2. The incorporation of TiO₂ in the coating led to an improvement in the crystal size and enhanced the corrosion resistance and microhardness property of the composite coating as compared to when Al₂O₃ or both are used with cerium.
3. The enhancement in corrosion resistance was due to the physical barriers produced by TiO₂ to the corrosion process by filling crevices and gaps on the surface of the zinc coatings.
4. This work has established that a Zn-TiO₂-CeO₃ coating on mild steel can be used to enhance the corrosion and hardness values.

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