CORROSION BEHAVIOR OF LOW-CARBON STEEL COATED WITH DIFFERENT TYPE OF TiO_2/ZrO_2 LAYERS

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Abstract

Two type of multilayer structures based on ZrO_2 coatings deposited on TiO_2 were applied on low carbon steel and their structure, composition and anticorrosion properties were evaluated in 5%NaCl salt medium. The phase composition, morphology and the elemental distribution of the coatings were investigated using X-ray diffraction analysis, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and energy dispersive X-ray analysis (EDX). The corrosion performance of the coatings was evaluated by potentiodynamic polarization measurements (PD). The zirconia/titania mixed oxide coating exhibited an enhanced corrosion resistance than those of the low carbon steel as indicated by the reduced current density, probably due to the presence of amorphous structure on the layers and dense surface without visible cracks and pits (barrier effect).

Keywords: *corrosion protection, dip coating, barrier properties, morphology*

1. INTRODUCTION

Steel is one of the most important and commonly used structural materials in the world. It is used practically in every sphere of daily life as well as in the almost whole industrialized world. However, steel cannot be regarded as a single product alone since various types are produced depending on their composition and percentage content.

Low carbon steels are iron-carbon alloys, the latter containing up to about 0.25 - 0.3 wt. % carbon in their composition. Generally, they are neither too brittle nor extremely ductile and their microstructure consisted mainly of ferrite and perlite. Due to the ease of fabrication, good availability and relatively low price these steels are base materials to be used for different applications - in automobile body panels, bolts, fixtures, seamless tubes, steel plates etc. [1].

Very often structures are subjected to extreme environmental conditions. Under the action of temperature changes, highly polluted media, such as those containing chlorine ions, the process of breaking down steels is greatly accelerated. Chloride ion is one of the most significant natural contaminant in marine and other environment which plays a main role in the corrosion process of the structural steel. The appearance of local corrosion, which can rapidly develop into the depth of the steel under the action of aggressive chlorine ions, could lead to irreversible damage and breakage of entire structures [2,3]. For all the reasons outlined above, different approaches for corrosion protection of these widely used materials are sought.

In recent decades, deposition of different nanosized oxide coatings on the base of ceria, titania, zirconia is a promising way to ensure effective corrosion protection of the steel. Currently, several deposition techniques are commonly used to produce oxide coatings: sol–gel deposition [4], pulsed laser deposition [5], chemical vapor deposition [6] etc. Among them the sol-gel method offers the

possibility to control the composition, microstructure, porosity etc. of the nanosized materials using different precursors, thermal treatments or additives in the sol.

The sol–gel method is widespread approach to produce multilayers at a lower cost than vacuum techniques at low temperatures. It can be easily combined with other film deposition methods. In addition, the method is waste-free. It can be used to produce nanostructured films with different thickness (typically 200 nm to 10 μm in overall). Moreover, ZrO_2 based ceramic is a popular alternative to alumina as dental bioceramic due to its excellent physical-chemical and also mechanical properties [7–9].

Zirconium dioxide coatings have been reported to promote excellent biocompatibility and superior corrosion protection as well as wear and tribological resistance 10]. The low cost, high hardness, chemical stability, good optical, antibacterial, photo-electrochemical properties and barrier action of TiO_2 coatings provide their effectiveness in different technological areas [11,12]. In this study, two type of TiO_2/ZrO_2 based sol gel multilayer systems were deposited using the dip coating technique. Their corrosion resistance and protective ability were evaluated by application of potentiodynamic polarization method in model test medium the latter containing chloride ions as corrosion activators.

2. MATERIALS AND METHODS

2.1. Materials

Two types of multilayer coatings were deposited and characterized as follow: the first type consisting of 3 under-layers of TiO_2 and top single layer of ZrO_2 (denoted as TZ1) and the second one, consisting of single TiO_2 layer and top three layers of ZrO_2 (denoted as TZ3). Low carbon steel plates (C- 0.05–0.12; S ≤ 0.04; P ≤ 0.35; Mn - 0.25–0.5; Cr ≤ 0.1; Si ≤ 0.03; Ni ≤ 0.3; Cu ≤ 0.3; As ≤ 0.08; Fe-balance) with sizes 20 x 10 x 1 mm were used as substrates. The latter were cleaned ultrasonically in ethanol before deposition.

Titania based coatings were prepared from "Sol T": titanium tetrabutoxide (TB) was dissolved in isopropanol and acetacetone. (0.4 M/L). Zirconium based coatings were obtained from Zr butoxide; $Zr(OC_4H_9)_4$ and small quantity of nitric acid were dissolved in 2-propanol, after that small quantity of acetic acid and acetylacetone were added as complexing agents. Finally, 5 wt% polyethylene glycol (Mw=400) was added as a structure directing agent. The obtained sol was denoted as "Sol Z".

The substrates were dipped in Sol T solution for 10 s to obtain better wettability, after that were withdrawn with rate 30 mm/min. After each deposition, the samples were dried consecutively at 100ºC and 200ºC for 1 h, respectively. The dipping-drying procedure was repeated three times for structure TZ1 and one time for structure TZ3. Then the deposits were dipped into Sol Z. The dipping and drying were repeated one/three times for TZ1 and TZ3 samples, respectively. The final treatment of the samples was carried out at 500ºC with heating rate of 5ºC/min.

2.2. Methods

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus). The surface topography was studied by means of Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc.) The scanning rate was set at 1 Hz. Subsequently, all the images were flattened by means of the Nanoscope software. The chemical composition and morphology was studied by SEM/EDX analyses (JEOL JSM 6390 and INCA Energy 350 unit, Tokyo, Japan).

The anticorrosion and protective properties of the multilayer systems were analyzed using the potentiodynamic polarization test. The curves were performed for characterization of the corrosion and anodic behavior as well as for evaluation of the corrosion behavior of the multilayer coating systems at conditions of external polarization in the model test medium using a VersaStat 4 (PAR) unit (Princeton Applied Research, Oak Ridge, TN, USA). The investigations were carried out in a three-electrode electrochemical cell of 250 mL volume at a scan rate of 1 mV/s. Counter-electrode is platinum wire and saturated calomel electrode (SCE) is used as a reference electrode. Prior to the start

of the experiment, the samples were kept in the model medium at open circuit potential (OCP) conditions during 15 min in order to stabilize their corrosion potential values.

The investigations were held in a model corrosion medium of 5wt.% NaCl solution at pH 6.7 and at ambient temperature. The reproducibility of the tests is an average of 5 samples per sample type.

3. RESULTS

Chemical composition of both multilayer structures evaluated by EDAX analysis is shown in Table 1.

Code	O, at%	Ti , at%	Zr, at%	Fe, at%
TZ1	65.36	4.16	1.94	28.54
TZ3	66.82	0.89	3.26	29.03

Table 1. Chemical composition of the multi-layers, evaluated by EDX analysis

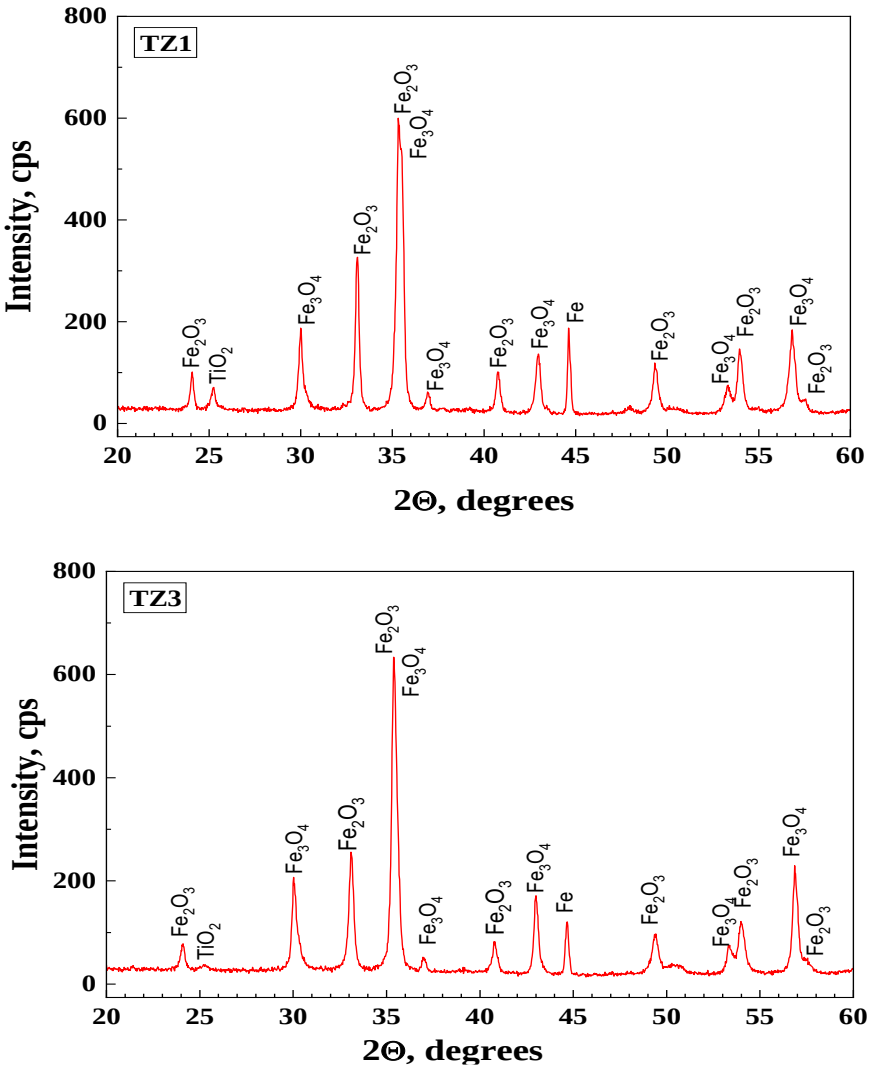


Fig. 1. XRD patterns of samples TZ1 (up) and TZ3 (down)

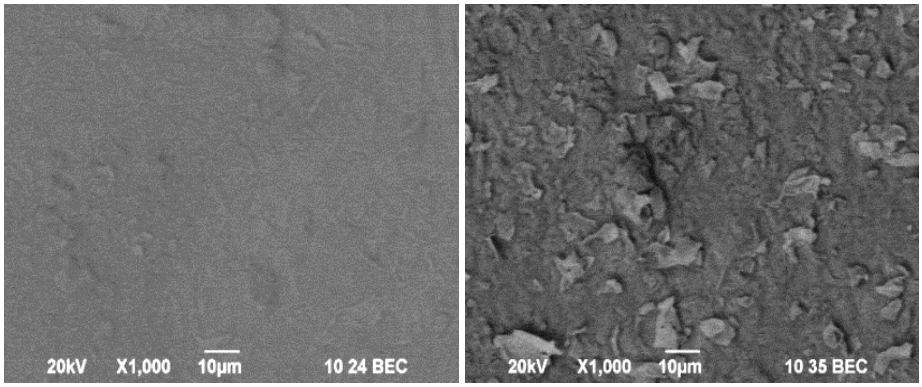


Fig. 2. Surface morphology of coatings TZ1 (left) and TZ3 (right)

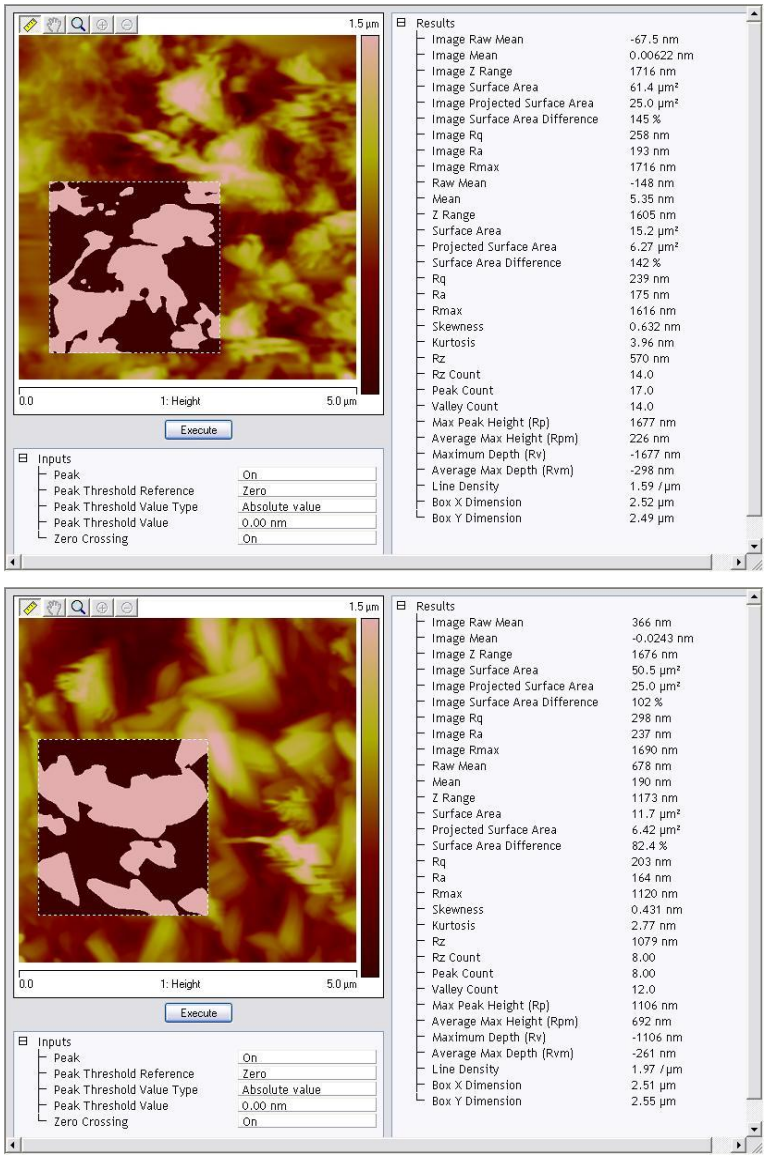


Fig. 3. 2D topography of coatings TZ1 (up) and TZ3 (down)

In the XRD patterns of both investigated structures the peaks, confirm the presence of two compounds/iron oxides - magnetite and hematite phases. This result is probably due to the oxidation of the substrate during the thermal treatment (Figure 1). Nevertheless, the peak which belongs to anatase phase of TiO_2 in the both patterns is well visible and can be registered especially in the case of TZ1. This result follows most probably from the type of the multilayer system as a whole due to three layered TiO_2 coatings. Because no ZrO_2 crystallographic phases were detected in the both of multilayer structures, one can conclude that zirconia layer possesses amorphous structure. Similar results have been presented by Bu et al. for titania-zirconia composite films [13]. Another researchers have revealed that the binary TiO_2–ZrO_2 remain in the amorphous phase even after calcination at 450◦C [14]. According to [15] zirconia-titania composite particles do not contain any segregated phases such as monoclinic/tetragonal zirconia or anatase/rutile titania up to 600°C.

The SEM images of both structures revealed a surface morphology homogeneously covered with the TiO_2-ZrO_2 multilayer systems (Fig. 2). The surface of the sample TZ1 looks more random while this of TZ3 seems to be rougher. No visible cracks or other surface defects can be registered. Figure 3 shows the two-dimensional AFM topography of the investigated titania/zirconia multilayers. The pictures reveal a columnar growth of zirconium dioxide on the coated low carbon steel substrate. It can be also registered from the figures, that the coatings are dense, without visible cracks. Although agglomeration of some particles can be observed at certain regions in the coating TZ3, the latter covers completely the carbon steel substrate.

Potentiodynamic polarization investigations in the selected model corrosion medium are demonstrated in Figure 4. The corrosion current density value of TZ3 sample is about $2{,}6.10^{-7}$ A/cm^2. Contrary to this, the same parameter of TZ1 coating is much higher - $3{,}8.10^{-6}$ A/cm^2. For comparison, the corrosion current density of the low-carbon steel sample is $5{,}1.10^{-6}$ A/cm^2. The corrosion potential of both multilayer systems also differ – that of TZ3 is more positive (-0,56 V) while that of TZ1 is about -0,61 V. The corrosion potential of the bare steel substrate is the negative one and appears at -0,7 V.

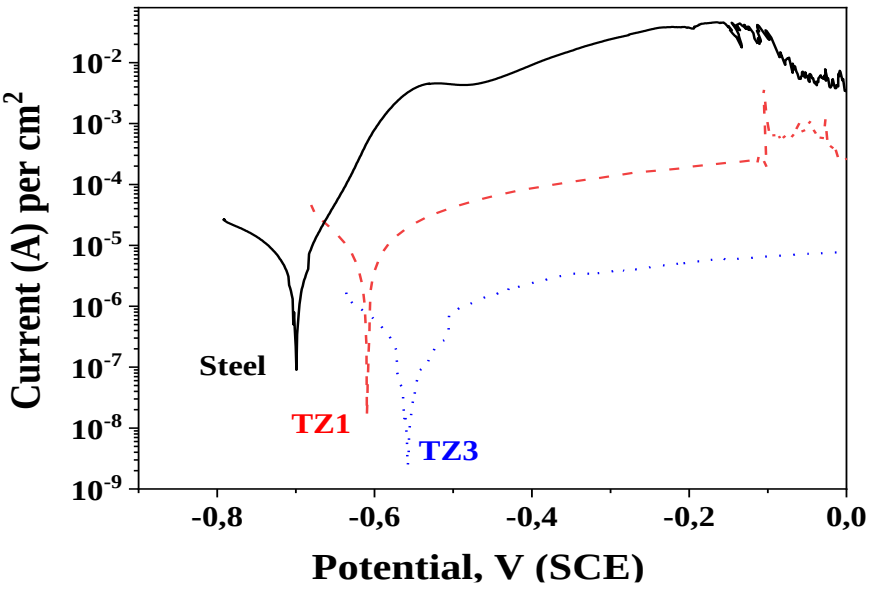


Fig. 4. Potentiodynamic polarization curves in 5% NaCl medium of Steel, TZ1 and TZ3.

The anodic branch of TZ1 coating is placed at higher anodic current density values compared to TZ3 sample and in addition, some oscillations can be registered for it in the potential area more positive than –0,1 V.

These results (carried out at external polarization) allows to argue that TZ3 sample demonstrates better protective ability and higher corrosion resistance in that medium compared to the other investigated coating – TZ1, which, however, also presents good protection toward the steel substrate.

4. DISCUSSION

Both of the oxide layer structures investigated in this paper exhibit enhanced corrosion resistance in model salt medium due to their better protective properties compared to monolayer coatings. This type of coatings combines the advantages of the single oxides such as: good barrier properties, good adhesion to steel substrate [16] as well as high electrical resistivity and mechanical parameters [17] of TiO_2 layer and the high corrosion and wear resistance as well as the chemical stability of ZrO_2 as a top layer [18].

Most probably, these characteristics seem to be the reason for better barrier properties of the multi-layer system TZ3 (with three consecutively deposited zirconia layers) than the TZ1. In addition, the amorphous structure of the outer zirconia layer deteriorates the ion and electron conduction, thus retarding cathodic or anodic electrochemical processes due to inhibition of intercrystalline corrosion between the grains [19]. According to literature the presence of amorphous structure of TiO_2-CeO_2 composite films improves the barrier properties [20]. It must be also bearing in mind that the relatively dense structure of the multylayers obtained induces higher anticorrosion behavior. Similar results have been presented by Holgado et al., which have proposed that the corrosion–protective effect of the ZrO_2 coatings is due to their high density and partial amorphous character of the films [21].

5. CONCLUSIONS

The multilayer titania/zirconia coatings with 2 different arrangements of the oxide layers were coated over low carbon steel surface by sol–gel dip-coating method. The surface and micro-structural analysis confirmed the presence of zirconium and titanium oxide over the coated surface. The coatings are amorphous with relatively dense surface morphology. The anti-corrosion properties of the multilayer coating systems was evaluated using 5% NaCl solution as a model medium. The low carbon steel coated with both type of multilayer structures showed higher corrosion resistance than the bare steel in that medium.

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