

Environmentally-Friendly Anticorrosive Layered Zirconia/Titania/Low-Carbon Steel Structures [†]

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Abstract: Improved corrosion protection of low-carbon steel was achieved by barrier non-toxic sol-gel multilayered structures composed of a ZrO₂ top coating and TiO₂ underlayers. The zirconium precursor solution was maintained as constant, whereas the TiO₂ solution composition was modified with two different types of polymers, which were added separately to the starting titanium solution. The phase composition, morphology and corrosion protective properties were analyzed by X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hydrophobicity properties were evaluated by measuring the contact angle with a Ramé-Hart automated goniometer. The potentiodynamic polarization technique was used to determine the corrosion resistance and protective ability of the coatings in a 5% NaCl solution. Both polymeric modifications, as compared to the non-modified titania layer, demonstrated positive effects on the corrosion properties of the structures at conditions of external polarization. Due to the amorphous structure of the zirconia layer and its relatively dense, hydrophobic surface, all of the samples extended the service life of low-carbon steel in a model corrosion medium. The feasibility of the sol-gel deposition method makes it possible to prepare oxide coatings with appropriate surface properties, which ensures high corrosion resistance.

Keywords: corrosion; barrier coatings; anti-corrosion performance; dip coating

1. Introduction

Low-carbon structural steels are widely used in the chemical and civil engineering fields due to their advantages of low cost, manufacturing flexibility and availability. Carbon steels have ferrite–perlite microstructures and usually contain C and Mn (Mn up to 2 wt%, C from 0.02 to 0.5 wt% and Si up to 0.5 wt%). During their operation, these materials are often subject to corrosion attack as a result of their interaction with surrounding media, as well as low overvoltage of hydrogen and/or low overvoltage of the ionization process on the iron surface. This leads to an accelerated corrosion process and the faster destruction of the latter. The presence of oxidants in the surrounding media has a strong influence on the corrosion potential value and on the corrosion rate of the iron. For example, in slightly acidic and neutral aqueous solutions, low soluble by-products of corrosion (well known in everyday practice as “rust”) are formed. Some of them have weak protective properties, but others can successfully defend the substrate for a certain

period of time. Generally, low-carbon steels (mild steels) are distinguished by not-very-well-expressed corrosion resistance. That is the reason to look for and to apply appropriate means of corrosion protection (for example, inhibitors, coatings etc.) during their operation at different conditions.

Various types of protective coatings have been developed to enhance the life span of carbon steel products such as organic monolayer [1], glass coatings [2] and ceramic coatings [3]. Nanosized oxide coatings possess good thermal and electrical properties, as well as higher resistance to oxidation, corrosion and wear than metals. Recently, the corrosion resistance of TiO_2 [4,5], SiO_2 [6], Al_2O_3 [7] and ZrO_2 [3] coatings have been studied. A variety of synthesis methods, such as the sol-gel method, hydrothermal method, direct oxidation method, electrodeposition, physical vapor deposition etc., have been developed for the synthesis of TiO_2 nanostructures, and their anti-corrosion properties have been investigated [8–10]. Among them, the sol-gel method has many advantages; it offers easy control of the microstructure and requires low-cost equipment, and it is a waste-free method, which is environmentally and economically more acceptable than the other deposition methods. Zirconium dioxide coatings are widely used in different areas, and especially as barrier anticorrosive coatings, due to their excellent physical and chemical properties [11]. The low cost, high hardness, chemical stability and good optical, photo-electrochemical and protective properties of TiO_2 coatings provide their effectiveness in various technological areas [12]. The common advantages of both oxides are their non-toxicity and biocompatibility. The aim of this study is to obtain environmentally-friendly $\text{TiO}_2/\text{ZrO}_2$ multilayers, deposited on low-carbon steel using the waste-free sol-gel method, that exhibit high corrosion resistance.

2. Materials and Methods

Three types of multilayer titania–zirconia protective coating systems, each of which consisted of 3 underlayers of TiO_2 (sequentially applied) and a top single layer of ZrO_2 , were deposited by the sol-gel method on low-carbon steel substrates ($\text{C} = 0.05\text{--}0.12$; $\text{S} \leq 0.04$; $\text{P} \leq 0.35$; $\text{Mn} = 0.25\text{--}0.5$; $\text{Cr} \leq 0.1$; $\text{Si} \leq 0.03$; $\text{Ni} \leq 0.3$; $\text{Cu} \leq 0.3$; $\text{As} \leq 0.08$; Fe -balance). The substrates were cleaned ultrasonically in ethanol before deposition. Titania-based coatings were prepared from three different types of sols. Sol A contained titanium tetrabutoxide (TB), which was dissolved in isopropanol and acetacetone (0.4 M/l). Sol B also contained a small quantity of polymeric modifier polyoxyethylene (20) sorbitan monooleate (Tween 80), while Sol C contained ethylcellulose. Zirconium-based coatings were obtained from Zr butoxide; $\text{Zr}(\text{OC}_4\text{H}_9)_4$ and a small quantity of nitric acid were dissolved in 2-propanol. Acetic acid and acetylacetone were added as complexing agents. Finally, 5 wt% polyethylene glycol ($M_w = 400$) was added as a structure directing agent. The substrates were dipped in each of sols A, B and C and were withdrawn at a rate of 30 mm/min. After each deposition, the samples were dried consecutively at 100 °C and 200 °C for 1 h. The dipping–drying procedure was repeated three times. Then the deposits were dipped into zirconium solution. The final treatment of the samples was carried out at 500 °C with a heating rate of 5 °C/min. At the end of this process, sample A consisted of 3 underlayers of TiO_2 obtained from Sol A; sample B, of 3 underlayers of TiO_2 obtained from Sol B; sample C, of 3 underlayers of TiO_2 obtained from Sol C. As mentioned above, all these systems were finished with a top single layer of ZrO_2 . The phase compositions of the samples were studied by X-ray diffraction (XRD) with $\text{CuK}\alpha$ -radiation (Philips PW 1050 apparatus). The surface topography was studied by means of an atomic force microscope (AFM) (NanoScopeV system, Bruker Inc., Billerica, MA, USA). 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 were studied by SEM/EDX analyses (JEOL JSM 6390 and INCA Energy 350 unit, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was applied to investigate the chemical composition and electronic structure of the films' surfaces. The measurements were carried out on an AXIS Supra electron spectrometer (Kratos Analytical Ltd., Manchester, UK) using achromatic $\text{AlK}\alpha$ radiation with

a photon energy of 1486.6 eV and a charge neutralization system. The binding energies (BE) were determined with an accuracy of ± 0.1 eV, using the C1s line at 284.6 eV (adsorbed hydrocarbons). The chemical composition in the depth of the films was determined by monitoring the areas and binding energies of C1s, O1s, Ti2p and Zr3d photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd., the concentrations of the different chemical elements (in atomic %) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors. Contact angle measurements were performed with a Ramé-Hart automated goniometer model 290 with DROPimage advanced v2.4 (Succasunna, NJ, USA) at room temperature. Drops of 2–5 μL were formed and deposited with a Ramé-Hart automatic dispensing system. 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 process and protective properties 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. The counter-electrode was platinum wire, and a saturated calomel electrode (SCE) was 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 for 15 min in order to stabilize their corrosion potential values. The investigations were held in a model corrosion medium of 5 wt% NaCl solution at pH 6.7 and at ambient temperature. The reproducibility of the realized investigations was an average of 5 samples per sample type.

3. Results and Discussion

3.1. Phase Structure

The presence of two compounds/iron oxides, magnetite and hematite phases, were registered by XRD analyses of all of the coating (Figure 1). This result was probably due to the oxidation of the substrate during the thermal treatment. Nevertheless, the peak that belongs to the anatase phase of TiO_2 is well visible, which is due to the type of the multilayer system consisting of three layered TiO_2 coatings. It could be supposed that the zirconia layer possessed an amorphous structure, because zirconia crystallographic phases were not registered. Several research groups have also revealed that the amorphous phase of the composites on the base of TiO_2 and ZrO_2 is stable after treatment to 450 $^\circ\text{C}$ [13] and even at 600 $^\circ\text{C}$ [14].

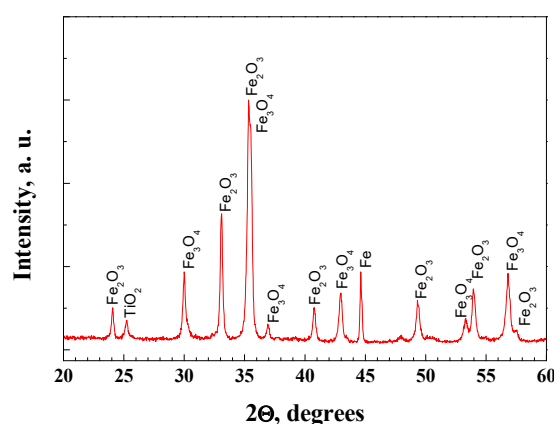


Figure 1. Typical XRD pattern of multilayer structure A.

3.2. Surface Morphology

The SEM images of the investigated structures reveal relatively homogeneous dense morphology without visible cracks. A few secondary small crystalline particles were formed on the surface (Figure 2). Similar observations can be made from the AFM images in Figure 3.

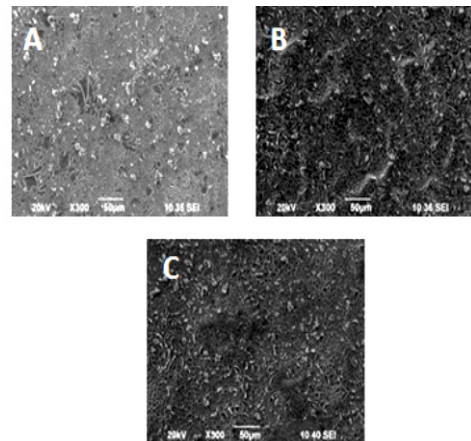


Figure 2. SEM photographs of the multilayer structures: (A) 3 layers TiO_2 (sol A) and top ZrO_2 layer; (B) 3 layers TiO_2 (sol B) and top ZrO_2 layer; (C) 3 layers TiO_2 (sol C) and top ZrO_2 layer.

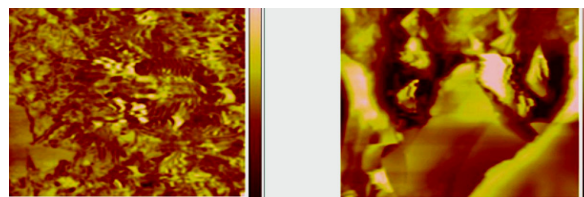


Figure 3. AFM 2D images of multilayer structures A (left) and C (right).

3.3. XPS Analyses of the Surface Composition

The XPS results show that peaks of C1s, O1s, Zr3d, Ti2p and Fe2p were registered on the surface. The oxygen spectra consist of three components. The first one, at 530 eV, corresponds to oxygen bound to metals, while the second and third ones, at 531.6 eV and 533.4 eV respectively, are attributed to adsorbed hydroxyl groups and surface water (Figure 4). The zirconium spectra are decomposed into several peaks associated with ZrO_2 (with binding energies 182.7 eV for $\text{Zr3d}_{5/2}$ peaks and 185.2 eV for $\text{Zr3d}_{3/2}$ peaks) and ZrOH (with binding energies 184.0 eV for $\text{Zr3d}_{5/2}$ and 186.7 eV for $\text{Zr3d}_{3/2}$). 1.4 at% TiO_2 and 13 at% Fe_2O_3 are also registered on the surface. From the areas of the deconvoluted oxygen peaks, it can be concluded that the amount of hydroxyl groups is the largest in multilayer C.

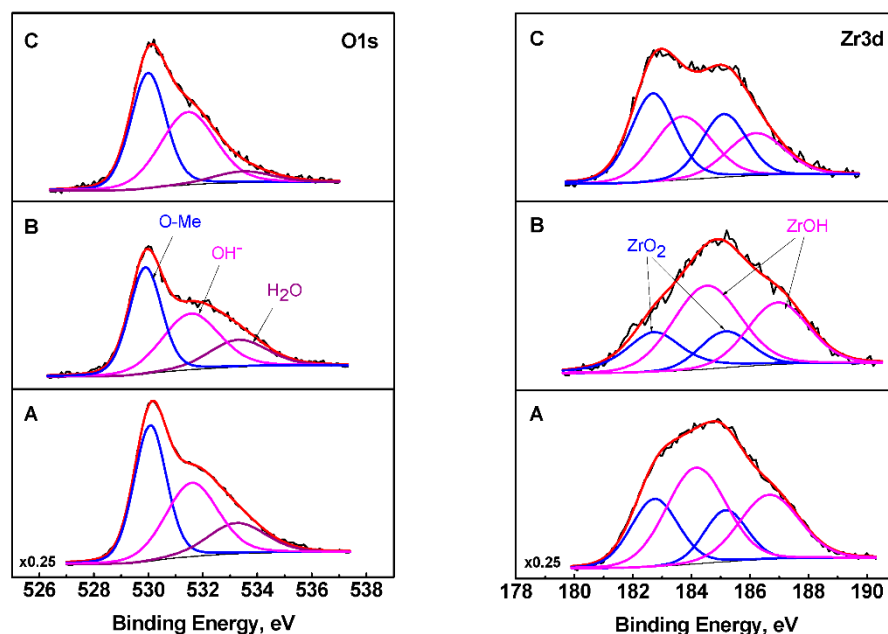


Figure 4. O1s and Zr3d core level spectra of the multilayered structures after deconvolution, where: (A) 3 layers TiO₂ (sol A) and top ZrO₂ layer; (B) 3 layers TiO₂ (sol B) and top ZrO₂ layer; (C) 3 layers TiO₂ (sol C) and top ZrO₂ layer.

3.4. Contact Angle Measurements

The measurement of the contact angles of the layers revealed that all of the studied multilayers exhibited hydrophobic properties (Figure 5). It has to be noted that the contact angle value is not dependent on the composition of the titania precursor solution.

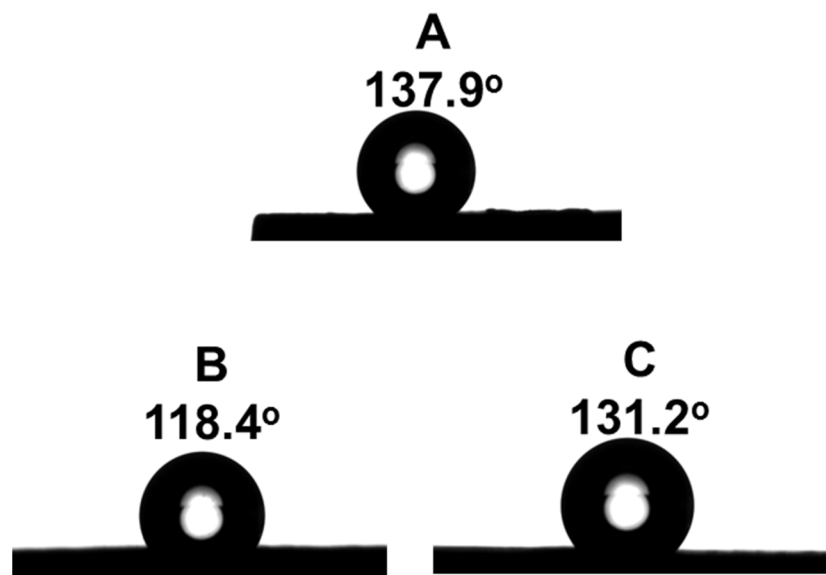


Figure 5. Contact angles of the multilayer structures. (A) 3 layers TiO₂ (sol A) and top ZrO₂ layer; (B) 3 layers TiO₂ (sol B) and top ZrO₂ layer; (C) 3 layers TiO₂ (sol C) and top ZrO₂ layer.

3.5. Corrosion and Anodic Behavior of the Structures Evaluated by Potentiodynamic Curves

The PD curves of the multilayer structures are demonstrated in Figure 6. It is well visible that all the systems had close corrosion potentials (between -0.605 V and -0.611 V, respectively), which could be expected as a result of their nature and composition. More interesting is the anodic branch of the curves. The registered corrosion current densities

of the investigated systems were as follows: for multilayer A, 8.1×10^{-6} A/cm²; for multilayer B, 4.3×10^{-6} A/cm²; for multilayer C, 2.3×10^{-6} A/cm². In addition, as a result of the applied external anodic polarization, multilayer A presented higher anodic current densities compared to B and C (up to about one order) in the whole potential area during the investigation. These observations led to the conclusion that the application of some selected polymers positively affected the corrosion resistance properties of the sol-gel coatings in that medium, ensuring their lower current densities in the anodic region.

The oxide layer structures investigated in this paper exhibited enhanced resistance in a corrosive salt medium due to their better protective properties compared to monolayer coatings. This type of structure combined the advantages of both single oxides. This includes the good barrier properties, adhesion to steel substrate [15] and high electrical resistivity and mechanical parameters of the TiO₂ layers [16]. On the other hand, the ZrO₂ top coating possessed high corrosion and wear resistance as well as chemical stability [3]. In addition, the amorphous structure of the outer zirconia layer deteriorated ion and electron conduction, thus retarding cathodic or anodic electrochemical processes due to inhibition of intergranular corrosion between the grains (IGC) [17]. According to literature, the presence of the amorphous structure of titania-based composite films improves protective properties [18].

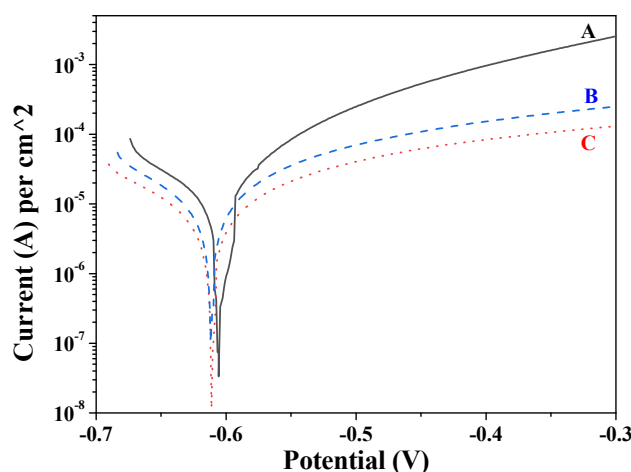


Figure 6. Potentiodynamic polarization curves of the multilayers in the model test medium.

Similar results were presented by Holgado et al., which proposed that the corrosion-protective effect of the ZrO₂ coatings was due to their high density and partial amorphous character of the films [19]. It must be kept in mind that the relatively dense, amorphous structure combined with the hydrophobic properties of the multilayers obtained induced higher anticorrosion behavior.

4. Conclusions

Multilayer titania/zirconia coatings, where three different titanium precursor solutions were used for TiO₂ layers, were coated over low-carbon steel by a sol-gel dip-coating method. Surface and microstructural analysis confirmed the presence of zirconium and titanium oxide over the substrate. The coatings were amorphous with relatively dense surface morphology. The anti-corrosion properties of the multilayer coating systems were evaluated using 5% NaCl solution as a model medium. The polymer addition into titania solution led to the formation of multilayer structures with lower current densities in the anodic region, ensuring better anti-corrosion performance than those consisting of non-modified TiO₂ underlayers. It could be supposed that the good protective properties of the multilayers were due to their amorphous, dense surfaces and hydrophobic nature.

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