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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 by ZrO_2 top coating and TiO_2 underlayers. Zirconium precursor solution was maintained constant, whereas, the TiO_2 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 the measuring of the contact angle with Ramé-Hart automated goniometer. 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 effect on the corrosion properties of the structures at conditions of external polarization. Due to amorphous structure of zirconia layer with relatively dense, hydrophobic surface of all of the samples extend the service life of low carbon steel in model corrosion medium. The feasibility of the sol gel deposition method makes 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 chemical and civil engineering fields, due to their advantages: low cost, manufacturing flexibility, availability. The carbon steels have ferrite-perlite microstructure and contain usually C and Mn (Mn up to 2 wt% and carbon 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 the surrounding media as well as due to low overvoltage of hydrogen and/or low overvoltage of the ionization process on the iron surface. This leads to accelerated corrosion process and faster destruction of the latter. The presence of oxidants in the surrounding media renders principally a strong influence on the corrosion potential value and on the corrosion rate of the iron, respectively. For example, in slightly acidic and neutral aqueous solutions, low soluble by-products of corrosion (well known in the everyday practice as "rust") are formed. Some of them have weak protective properties but other can successfully defend the substrate for a

certain period of time. Generally, low carbon steels (mild steels) distinguish with not very well expressed corrosion resistance. That is the reason to look for and to apply appropriate means of corrosion protection, for instance 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, high 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 such as 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: easy control of the microstructure, low cost equipment and it is 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, 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 the non-toxicity and the biocompatibility. The aim of this study is to obtain environmentally-friendly TiO_2/ZrO_2 multilayers, deposited on low carbon steel using waste-free sol gel method, which exhibit high corrosion resistance.

2. Materials and Methods

Three types of multilayer titania-zirconia protective coating systems each of which consist of 3 underlayers of TiO_2 (sequentially applied) and a top single layer of ZrO_2 were deposited by sol gel method on low carbon steel substrates (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). The substrates were cleaned ultrasonically in ethanol before deposition. Titania based coatings were prepared from three different types of sols. Sol A contains titanium tetrabutoxide (TB) the latter being dissolved in isopropanol and acetacetone (0.4 M/l). Sol B contains additionally small quantity of polymeric modificator Polyoxyethylene (20) sorbitan monooleate (Tween 80) while Sol C—ethylcellulose. Zirconium based coatings were obtained from Zr butoxide; $Zr(OC_4H_9)_4$, small quantity of nitric acid were dissolved in 2-propanol. Acetic acid and acetylacetone were added as complexing agents. Finally, 5 wt% polyethylene glycol (Mw = 400) was added as a structure directing agent. The substrates were dipped in every of sols A, B and C and were withdrawn with rate 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 heating rate of 5 °C/min Finally, the sample A consists of 3 underlayers TiO_2 obtained from Sol A; sample B—of 3 underlayers TiO_2 obtained from Sol B; sample C—of 3 underlayers TiO_2 obtained from Sol C. As mentioned above all these systems are finished with a top single layer of ZrO_2. The phase compositions of the samples were studied by X-ray diffraction (XRD) with Cu$K\alpha$-radiation (Philips PW 1050 apparatus). The surface topography was studied by means of Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc., Massachusetts, United States) 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). X-ray photoelectron spectroscopy (XPS) was applied to investigate the chemical composition and electronic structure of the films surface. The measurements were carried out on AXIS Supra electron-spectrometer (Kratos Analitycal Ltd., Manchester, UK) using achromatic Al$K\alpha$ radiation with a photon energy of 1486.6 eV and 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 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 are performed with 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 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. 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 5 wt% NaCl solution at pH 6.7 and at ambient temperature. The reproducibility of the realized investigations is 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 have been registered by XRD analyses of all of the coating (Figure 1). This result is probably due to the oxidation of the substrate during the thermal treatment. Nevertheless, the peak which belongs to 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 zirconia layer possesses amorphous structure, because zirconia crystallographic phases are not registered. Several research groups have been also revealed that the amorphous phase of the composites on the base of TiO_2 and ZrO_2 is stable after treatment to 450 °C [13] and even at 600 °C [14].

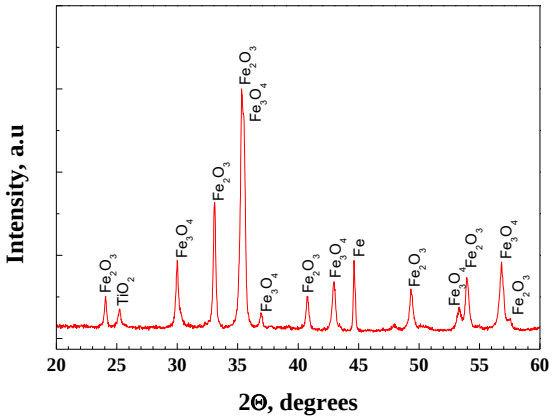

Figure 1. Typical XRD pattern of the multilayer structure A.

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 being formed on the surface (Figure 2). Similar observations can be made from the AFM images on Figure 3.

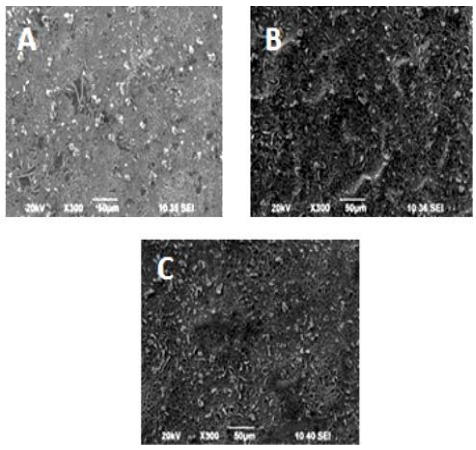

Figure 2. SEM photographs of the multilayer structures.

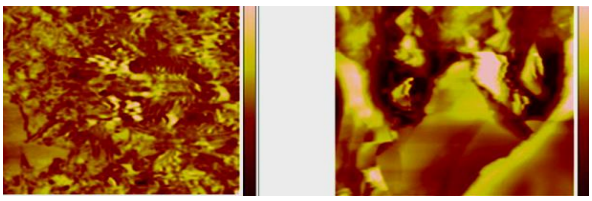

Figure 3. AFM 2D images of the multilayer structure A (left) and C (right).

3.3. XPS Analyses of the Surface Composition

The XPS results show that peaks of C1s, O1s, Zr3d, Ti2p and Fe2p are registered on the surface. The oxygen spectra consist of three components. The first one at 530 eV corresponds to oxygen bound to metals, the second and the third one at 531.6 eV and 533.4 eV 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 $Zr3d_{5/2}$ peaks and 185.2 eV for $Zr3d_{3/2}$ peaks) and ZrOH (with binding energies 184.0 eV for $Zr3d_{5/2}$ and 186.7 eV for $Zr3d_{3/2}$). 1.4 at.% TiO_2 and 13 at.% Fe_2O_3 are also registered on the surface, which are a results of the corrosion protection tests. From the areas of the deconvoluted oxygen peaks it can be concluded that the amount of hydroxyl groups is the largest in multilayer C.

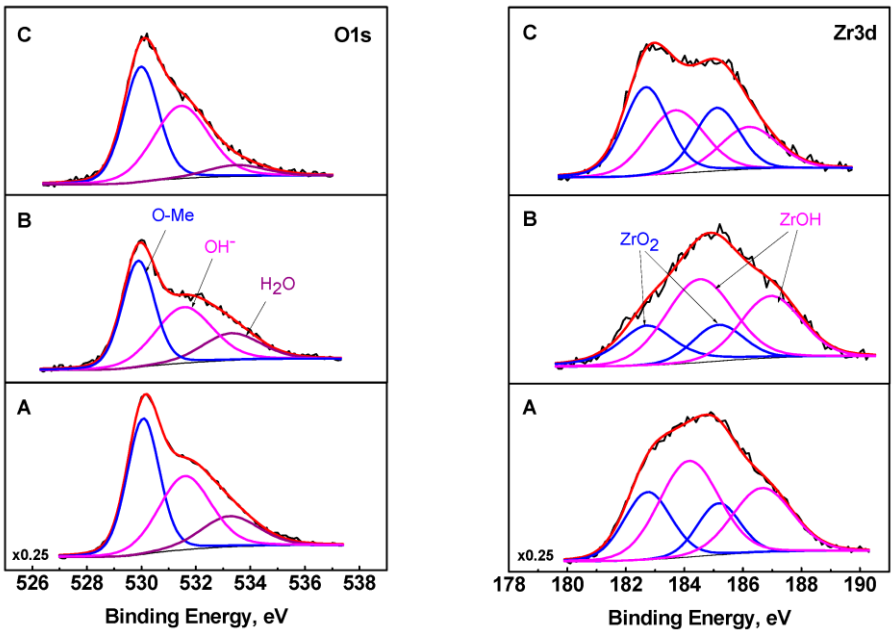

Figure 4. O1s and Zr3d core level spectra of the multilayered structures after deconvolution.

3.4. Contact Angle Measurements

The measurement of the contact angles of the layers revealed that all of the studied multilayers exhibit 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.

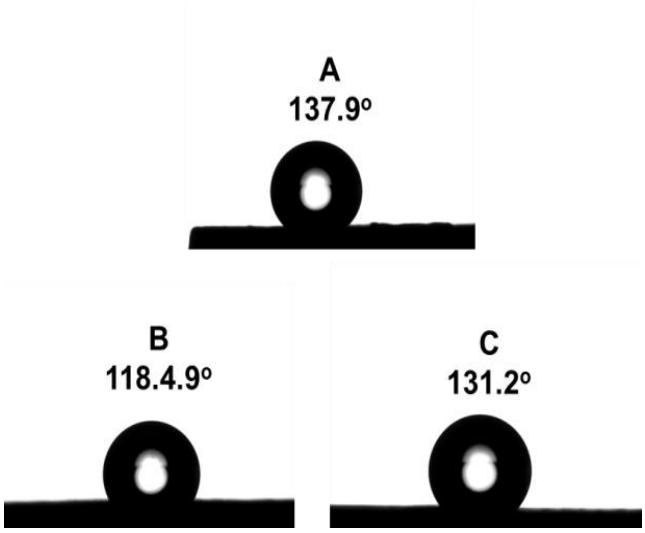

Figure 5. Contact angle of the multilayer structures.

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 have 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 are as follows: for multilayer A—8.1 × 10^{-6} A/cm^{-2}; for multilayer B—4.3 × 10^{-6} A/cm^{-2}; for multilayer C—2.3 × 10^{-6} A/cm^{-2}. In addition, as a result of the applied external anodic polarization multilayer A presents higher anodic current densities compared to B and C (up to about one order) in the whole potential area during the investigation. These observations lead to the conclusion that the application of some selected polymers affects positively 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 exhibit enhanced resistance in corrosive salt medium due to their better protective properties compared to monolayer coatings. This type of structures combines the advantages of the both single oxides: good barrier properties, adhesion to steel substrate [15] and high electrical resistivity and mechanical parameters of TiO_2 layer [16]. On the other hand ZrO_2 top coating possesses high corrosion and wear resistance as well as chemical stability [3]. 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 intergranular corrosion between the grains (IGC) [17]. According to literature the presence of amorphous structure of titania based composite films improves the protective properties [18].

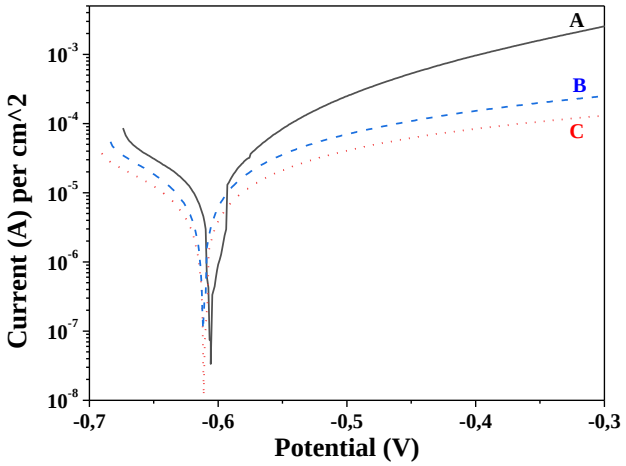

Figure 6. Potentiodynamic polarization curves of the multilayers in the model test medium.

Similar results have 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 [19]. It must be bearing in mind that the relatively dense amorphous structure with hydrophobic properties of the multilayers obtained induce higher anticorrosion behavior.

4. Conclusions

The multilayer titania/zirconia coatings where 3 different titanium precursor solutions were used for TiO_2 layers were coated over low carbon steel by sol–gel dip-coating method. The surface and micro-structural analysis confirmed the presence of zirconium and titanium oxide over the substrate. 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 polymer addition into titania solution leads to formation of the multilayer structures with lower current densities in the anodic region, ensuring better anti-corrosion performance than those, consisting of non-modified TiO_2 underlayer. It could be supposed that the good protective properties of the multilayers is due to their amorphous dense surface with hydrophobic nature.

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References

1. Meth, S.; Savchenko, N.; Koltypin, M.; Starosvetsky, D.; Groysman, F.A.V.A.; Sukenik, C.N. Corrosion studies of stainless steel protected by a TiO2 thin film deposited on a sulfonate-functionalized self-assembled monolayer. *Corros. Sci.* **2010**, *52*, 123–129.
2. Fu, G.; Wei, L.; Chang, X.; Cui, Y.; Wang, Y.; Yu, B.; LV, C.; Ye, S. A MgO–SiO_2–Al_2O_3–ZnO Ceramic-glass Coating to Improve the Anti-oxidation of Carbon Steel at High Temperature2018. *ISIJ Int.* **2018**, *58*, 929–935.

3. Stambolova, I.; Dimitrov, O.; Yordanov St Blaskov, V.; Vassilev, S.; Shipochka, M.; Boshkov, N. Preparation of newly developed CeO_2/ZrO_2 multilayers: Effect of the treatment temperatutre on the structure,and corrosion performance of stainless steel. *J. Alloys Comp.* **2019**, *806*, 1357–1367.
4. Yordanov St Stambolova, I.; Lakov, L.; Jivov, B.; Blaskov, V.; Vassilev, S. Efect of CeO_2 dopant on the structure and protection properties of TiO_2 sprayed coatings deposited on carbon steel. *J. Chem. Technol Metall.* **2018**, *53*, 1179–1185.
5. Yordanov, S.T.; Lakov, L.; Stambolova, I.; Blaskov, V.; Djakova, V.; Eliyas, A. Surface morphology and corrosion resistance of neodimum doped TiO_2. Sol-gel coatings. *Comptes rendus de l'Académie bulgare des Sciences* **2018**, *71*, 619–621.
6. Yu, Q.; Ma, X.H.; Wang, M.Z.; Yu, C.J.; Bai, T. Influence of embedded particles on microstructure, corrosion resistance and thermal conductivity of CuO/SiO_2 and NiO/SiO_2 nanocomposite coatings. *Appl. Surf. Sci.* **2008**, *254*, 5089–5094.
7. Feng, Q.Y.; Li, T.J.; Teng, H.T.; Zhang, X.L.; Zhang, Y.; Liu, C.S. Investigation on the corrosion resistance and oxidation of $Ni\text{-}Al_2O_3$ nano-composite coatings by sediment co deposition. *Surf. Coat Technol.* **2008**, *202*, 4137–4144.
8. Yun, H.; Lin, C.J.; Li, J.; Wang, J.R.; Chen, H.B. Low-temperature hydrothermal formation of a net-like structured TiO_2 film and its performance of photogenerated cathode protection. *Appl. Surf. Sci.* **2008**, *255*, 2113–2117.
9. Ohko, Y.; Saitoh, S.; Tatsuma, T.; Fujishima, A. Photoelectrochemical anticorrosion and self-cleaning effect of a TiO_2 coating for type 304 stainless steel. *J. Electrochem. Soc*. **2001**, *148*, B24–B28.
10. Karpakam, V.; Kamaraj, K.; Sathiyanarayanan, S. Electrosynthesis of PANI-nano TiO_2 composite coating on steel and its anti-corrosion performance. *J. Electrochem. Soc.* **2011**, *158*, C416–C423.
11. Xia, W.; Li, N.; Deng, B.L.; Zheng, R.; Chen, Y. Corrosion behavior of a sol-gel ZrO_2 pore-sealing film prepared on a micro-arc of aluminum alloy. *Ceram. Intern.* **2019**, *45*, 11062–11067.
12. Chen, X.; Mao, S. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and applications. *Chem. Rev*. **2007**, *107*, 2891–2959.
13. D Zou, H.; Lin, Y.S. Structural and surface chemical properties of sol–gel derived TiO_2–ZrO_2 oxides. *Appl. Catal. A* **2004**, *265*, 35–42.
14. Hu, M.; Payzant, Z.C.; Booth, E.A.; Rawn, K.R.; Hunt, R.D.; Allard, L.F. Ultrafine microsphere particleszirconium titanate produced by homogeneous dielectric-tuning coprecipitation. *J. Mater. Sci*. **2003**, *38*, 3831–3844.
15. Schiemann, D.; Alphonse, P.; Taberna, P.-L. Synthesis of high surface area TiO_2 coatings on stainless steel by electrophoretic deposition. *J. Mater Res*. **2013**, *28*, 2023–2030.
16. Jh Dhiflaoui, H.; Kaouther, K.; Larbi, A.B.C. Wear Behavior and Mechanical Properties of TiO_2 Coating Deposited Electrophoretically on 316 L Stainless Steel. *J. Tribol.* **2018**, *140*, 031603.
17. Kadhum, A.H.; Mohamad, A.B.; Hammed, L.A.; Al-Amiery, A.A.; San, N.H.; Musa, A.Y. Inhibition of mild steel corrosion in hydrochloric acid solution by new cumarin. *Materials* **2014**, *7*, 4335–4348.
18. Ghasemi, T.; Shahrabi, A.A.; Oskuie, H.H.; Sanjabi, S. Effect of heat treatment on corrosion properties of of sol–gel titania–ceria nanocomposite coating. *J. Alloys Comp.* **2010**, *504*, 237–242.
19. Holgado, J.P.; Pérez-Sánchez, M.; Yubero, F.; Espinós, J.P.; González-Elipe, A.R. Corrosion resistant ZrO_2 thin films prepared at room temperature by ion beam chemical vapor deposition. *Surf. Coat. Technol*. **2002**, *151–152*, 449–453.