Surface Morphological and Chemical Features of Anticorrosion ZrO$_2$–TiO$_2$ Coatings: Impact of Zirconium Precursor

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Abstract: Dense, highly textured, hydrophobic ZrO$_2$–TiO$_2$ (1:1) coatings with amorphous structure were prepared using the sol-gel method. Both organic and inorganic zirconium precursor salts were used. The present study dealt with the investigation of their protective ability in a selected model corrosive medium with chloride ions as corrosion activators. The coatings showed good anticorrosion performance during the test, which was demonstrated both by the weight loss method and potentiodynamic polarization curves. The samples were characterized by means of X-ray diffraction (XRD), Atomic Force Microscopy (AFM), contact angle measurements, Infrared spectroscopy (IRS), Scanning Electron Microscopy (SEM), Differential Thermal analysis (DTA-TG) and X-ray photoelectron spectroscopy (XPS). It was established that the extent of influence of some factors, like treatment temperature ($T_{tr}$) and type of zirconium precursor, was different. The PD curves of samples treated at 400 °C (A4 and B4, respectively) demonstrated an increased effect of the precursor in comparison to $T_{tr}$, since the application of organic Zr salt led to deterioration of the anodic passivation zones. Contrary to this, the coatings obtained from both the organic and inorganic Zr precursor salts with $T_{tr} = 500$ °C had similar corrosion efficiency, i.e., the influence of the precursor was minimized. All investigated coatings had no visible corrosion damage. It seems that some complex structural and surface parameters, such as amorphous dense structure, surface smoothness, hydrophobicity and the surface chemical composition (low hydroxyl groups content), were responsible for the increased anticorrosion properties of the composite films.

Keywords: composite sol-gel coatings; corrosion performance; hydrophobic properties; surface morphology; oxide films

1. Introduction

The global importance of corrosion-related durability challenges, especially in industry, requires a wide scope of scientific research work. Generally, corrosion can cause costly and dangerous damage of different important systems, as well as of major infrastructures. To the best of our knowledge, a great part of human health security and financial costs worldwide (including respective safety and environmental consequences) are corrosion-related. Despite the existing high level of academic potential and fundamental knowledge in the fields of electrochemistry and corrosion science, the situation regarding the protection of steel structures is not yet very optimistic. Therefore, investigations connected with the corrosion-protection of steel are of great importance. As it is well known, corrosion is a
diffusion-controlled process, which can be either concentrated in selected areas forming pits or cracks, or it can extend across a wide area on the surface.

Various approaches have been applied to limit the harmful effects of this phenomenon, for example, cathodic protection or reducing the activity of the aggressive medium by application of different inhibitors [1–5]. Another possibility is to provide passive protection by creating a physical barrier between the metals and their surrounding environment by using (i) chromium (III)-based or chromium-free conversion films, (ii) painting, (iii) hot-dip galvanizing, (iv) nanosized ceramic oxide coatings, etc. [6–10]. The unique physical, mechanical and chemical properties of the latter compared with those of their cast counterparts are due to their small grain size (<100 nm) and high volume fraction of grain boundaries.

Several investigators have tried to obtain and characterize the protective properties of these mainly amorphous materials, through which the latter have offered an attractive basis for improved corrosion resistance, which is due to the practical absence of linear and planar defects like dislocations and chemical inhomogeneity. A greater number of amorphous materials are also characterized by high mechanical strength and good surface quality. Some authors have noted that the amorphous structure could effectively influence the composition and compactability of the passive films in aggressive media containing Cl$^-\text{ions}$ as corrosion activators. The then-obtained films are more compact, having a lower defect density [11]. However, the demonstration of improved corrosion resistance of amorphous materials, compared to their crystalline counterparts, suffers from the fundamental drawback that it is difficult to achieve an amorphous structure and a crystalline single-phase material of the same alloy chemistry in most experimental and commercial systems [12,13]. According to [14] the surface reactivities of amorphous metals are certainly different from those of crystalline surfaces, and this parameter can be changed widely from a high activity to a low activity by controlling the composition. As it is well known, the amorphous structure exhibits a predominantly chemically homogeneous nature, which is due to the lack of defects which could possibly act as chemically active sites.

Ceramic coatings like TiO$_2$, ZrO$_2$, CeO$_2$, etc. have attracted considerable attention due to their ease of manufacturing, low cost, electrical properties, better mechanical stability as well as corrosion resistance [15]. Generally, the very fine particle sizes of the coatings ensure better blocking of the diffusion of the corrosive elements to the substrate.

TiO$_2$ has proved to be one of the most promising materials for various applications, such as solar energy conversion, fuel cells, paints and photocatalysts, especially in environmental remediation processes, due to its high chemical stability, availability and low cost. As TiO$_2$ has worse mechanical properties, it is usually mixed with some other oxides, especially ZrO$_2$, in order to increase its stability. Zirconia is widely used as a catalyst, since it exhibits acidic, basic, oxidizing and reducing properties. In addition, it is well known that the conductivity of TiO$_2$ and ZrO$_2$ is of the order of 10$^{-8}$ $\Omega \cdot m^{-1}$, which confirms their nature as insulators and leads to a better corrosion performance. It is known that the introduction of a second metal oxide (such as ZrO$_2$) into TiO$_2$ is a prospective way of modifying several physicochemical characteristics of bare oxide, such as textural properties, morphology, etc. [16]. The doping of TiO$_2$ with ZrO$_2$ improves several physical and chemical characteristics (like electron mobility, mechanical strength and thermal stability), prevents anatase–rutile transition [17] and decreases the titania particles sizes [18,19]. The mixture of ZrO$_2$–TiO$_2$ exhibits a higher thermal stability than that of the pure single oxides and has been extensively investigated in the field of acidic sites catalyzed by reactions or as a support of catalytically active species [20,21]. Titania–zirconia composites, as electrodes of dye-sensitized solar cells, have increased the optical band gap, thus leading to enhancement of solar energy conversion efficiency [22]. Miao et al. have reported the increased hardness of ZrO$_2$–TiO$_2$ composite films [23]. Other authors have been studying TiO$_2$–ZrO$_2$ multilayer thin films as humidity sensors [24]. Piwonski et al. have also revealed the positive effect of adding zirconia nanoparticles into TiO$_2$ coatings on the frictional behavior and wear resistance in comparison to bare TiO$_2$ [25]. Sudhaugas et al. have synthesized ZrO$_2$–TiO$_2$ composites on stainless steel, which offer both the biocompatibility and high
Our survey of the available literature concerning titania–zirconia corrosion-resistance coatings revealed that the data about the complex influence of the topography, X-ray structure and hydrophobicity on their barrier properties are incomplete. The present study was aimed at revealing to what extent the surface chemistry (stoichiometry, content of oxygen and hydroxyl groups), in addition to the above-mentioned factors, contributes to the enhancement of anticorrosion efficiency of composite films based on TiO$_2$–ZrO$_2$/stainless steel.

2. Materials and Methods

Two types of zirconium precursors were applied: (A). organic, zirconium n-butoxide (Zr(C$_4$H$_9$O)$_4$, Alfa Aesar, Haverhill, MA, USA), and (B) inorganic, zirconyl oxychloride (ZrOCl$_2$·2H$_2$O).

2.1. Sample Types
2.1.1. Samples Type A

Zirconium precursor solution “A” was prepared using Zr(C$_4$H$_9$O)$_4$, diluted with isopropanol. Thereafter, a small amount of acetyl acetone, as a stabilizer, and acetic acid, as a complexing agent, were added. The solution was stirred for 2 h in order to complete the reaction between alkoxide and acetic acid. Titanium butoxide (Ti(OBu)$_4$) and acetyl acetone were dissolved in 2-propanol to a 1 M solution, stirring vigorously at room temperature. The viscosity of the obtained salts was about 5–10 cP. The resulting sols were transparent and stable. The solutions were mixed at a ratio Ti:Zr = 50:50 (1:1). The procedure was repeated 5 times, after which the samples were divided into 2 groups, treated at 400 and 500 °C for 1 h and will be referred to here as A4 and A5, respectively.

2.1.2. Samples Type B

Zirconium precursor solution “B” was prepared using ZrOCl$_2$·8H$_2$O (p.a.) dissolved in ethanol and nitric acid; the latter was added to prevent hydrolysis. A small amount acetyl acetone was added, as a complexing agent, to the mixture, followed by stirring the solution for 2 h. The procedure described in step 1 was used to prepare the precursor solution for Ti. Both solutions were mixed at a ratio Ti:Zr = 50:50 (1:1). After ultrasonic cleaning of the steel substrates in ethanol for 10 min, they were immersed in each one of the respective precursor solutions, held for 10 s and then withdrawn at a rate of 30 mm/min. After each application, the samples were air-dried at 100 °C, after which the temperature was raised to 300 °C for 1 h. The samples were divided into 2 groups, treated at 400 and 500 °C for 1 h, and they will be referred to further as B4 and B5, respectively. Figure 1 presents the experimental scheme for deposition of the composite coatings.

2.2. Differential Thermal (DTA)/Thermogravimetric (TG) Analyses

The differential thermal analysis was accomplished on a combined DTA–TG apparatus LAB—SYSEVO 1600, manufactured by the SETARAM Company (Caluire, France). Synthetic air was used as the carrier gas: flow rate of 20 mL·min$^{-1}$; heating rate 10 °C/min and probe mass was 25 mg. The analyses were carried out proceeding within the interval from 25 to 800 °C. A corundum crucible and a Pt/Pt–Rh thermocouple were used.

2.3. XRD Studies

The phase compositions of the samples were studied by X-ray diffraction (XRD) using CuK$_a$-radiation ($\lambda = 0.154056$ nm at 40 kV; Philips PW 1050 apparatus, Amsterdam, The Netherlands).
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2.4. Infrared Analyses

The infrared spectra (4000–400 cm⁻¹ region) were registered in KBr pellets having a diameter of 13 MA, using a Thermo Scientific Nicolet iS5 Fourier-transform IR spectrometer (Thermo Scientific Co., Waltham, MA, USA) at a spectral resolution of 2 cm⁻¹.

2.5. SEM Studies

Scanning electron microscopy (SEM) micrographs were recorded on apparatus JEOL JEM-200CX (JEOL, Tokyo, Japan), work mode: Secondary Electrons Image (SEI) and accelerating voltage: 80 keV.

2.6. AFM studies

The surface topography was evaluated by means of an Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc., Birrica, MA, USA) operating in tapping mode in air. The scanning rate was set at 1 Hz. and the images were taken in the highest possible resolution mode of the AFM, 512 × 512 pixels in JPEG format using the NanoScope software (Bruker Inc., Birrica, MA, USA). AFM permits evaluation of the roughness of the sample surface and its standard deviation (\(R_q\)). The roughness analysis also gave the value of \(R_a\).

Images from three independent locations of the samples were taken for reproducibility purposes. From the applied roughness analysis, statistical values according to the relative heights of each pixel in a particular AFM image were calculated. The roughness analysis gave the value of \(R_a\), which is an arithmetic average of the absolute values \(Z_j\) of the surface height deviations, measured from the mean plane, i.e.,

\[
R_a = \frac{1}{N} \sum_{j=1}^{N} |Z_j| \tag{1}
\]

while the image \(R_q\) is the root mean square average of height deviations taken from the mean image data plane, expressed as:

\[
R_q = \sqrt{\frac{\sum_{j=1}^{N} Z_j^2}{N}} \tag{2}
\]
2.7. XPS Investigations

The measurements were carried out on an AXIS Supra electron-spectrometer (Kratos Analytical Ltd., Manchester, UK), using achromatic AlKα 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 C 1s line at 284.6 eV (adsorbed hydrocarbons). Using the commercially available data-processing software of Kratos Analytical Ltd., the concentrations of the different chemical elements (in at.%) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

2.8. Contact Angle Measurements

Contact angle measurements were performed with Ramé–Hart automated goniometer model 290, with DROPimage advanced v2.4 (Ramé–Hart instrument co., Succasunna, NJ, USA) at room temperature. Drops of 2–5 µL were formed and deposited by the Ramé–Hart automatic dispensing system. The corrosion resistance of the samples was estimated according to EN ISO 10289:2006 [27]. In order not to disturb the integrity of the test coating, the samples were washed several times with distilled water and dried before weighing.

2.9. Neutral Salt Spray (NSS) Tests

These tests were carried out in a special chamber (Q-Lab unit) and in a corrosive medium, i.e., salt spray obtained by spraying a 3.5 wt.% aqueous solution of NaCl (p.a.) with a pH value in the range 6.5–7.2. The operating temperature in the test chamber was maintained within 35 ± 2 °C (ISO 9227:2017) [28].

2.10. Potentiodynamic Investigations

These studies were performed in order to characterize the corrosion behavior of the samples of both groups (group A (A4 and A5) and group B (B4 and B5), respectively) in a model corrosive medium of 3.5% NaCl solution under conditions of external polarization (cathodic and anodic). The experiments were performed in a glass tri-electrode electrochemical cell having a volume of 300 mL. A saturated calomel electrode (SCE) was used as a reference electrode, and a platinum plate was applied as a polarizing one. The polarization of the test specimens was performed by the equipment "PAR VersaStat 4" (Ametek SI, Berwyn, PA, USA) at a sufficiently low potential scan rate of 1 mV/s.

3. Results

3.1. Differential Thermal (DTA)/Thermogravimetric (TG) Analyses

In order to determine the appropriate regime of thermal treatment of the composite coatings, at which they preserve their amorphous structure, we applied DTA/TG analyses to the precursor solutions A and B only, dried at 100 °C (Figure 2). The registered endothermic peak at 100 °C corresponded to the loss of adsorbed water. The observed four small exothermic peaks in the DTA curve of mixture A could have been due to the gradual decomposition of a greater amount of organic residues of the two metal alkoxides. According to the literature data [29–31], the decomposition of the single zirconium or titanium alkoxide proceeds within the interval from 400 to 500 °C, while in our case, the mixture ZrO2–TiO2 (1:1) remained amorphous up to 500 °C.

Other research groups have also revealed that the transition from the amorphous to crystalline phase occurs above 600 °C [32]. The registered exothermic peaks in the mixture B within the temperature interval of 250–550 °C could be assigned to the decomposition of organic groups and inorganic Zr salt, accompanied by a strong decrease of the mass. The exothermic peaks of 535 °C for sample A and 547 °C for sample B corresponded to the crystallization of ZrO2 and TiO2 from the amorphous mixtures, respectively. The peaks at 693 and 642 °C, registered in mixtures A and B, respectively, most probably corresponded to the crystallization of the ZrTiO4 phase.
According to the literature data [29–31], the decomposition of the single zirconium or titanium alkoxide proceeds within the interval from 400 to 500 °C, while in our case, the decomposition of organic groups and inorganic Zr salt, accompanied by a strong decrease of the mass, was not recorded, i.e., they had an X-ray amorphous phase after calcination at 450 °C [34] and even up to 600 °C [35].

The XRD spectra of the coatings (Figure 4) both showed an anatase phase, while the crystallographic phase peaks of ZrO$_2$ were not recorded, i.e., they had an X-ray amorphous structure. Similar results have been represented by Bu et al. for titania–zirconia composite films [33]. Other researchers have revealed that the binary TiO$_2$–ZrO$_2$ remains in the amorphous phase after calcination at 450 °C [34] and even up to 600 °C [35].
3.3. Infrared Analyses

Infrared spectroscopy was used to determine the rate and degree of hydrolysis and condensation, as well as the phase transformations in the gels (Figure 5). The absorption broad bands in both spectra at the 3000–3600 cm\(^{-1}\) region corresponded to the vibrational frequencies of OH groups, due to adsorbed water molecules and surface hydroxyl groups [36]. The bands within the region of 2850–2960 cm\(^{-1}\) corresponded to vibrational vibrations of the CH groups of the organic precursors (butoxy group of the precursor) [37]. According to the literature data, Ti (IV) butoxide (TBT) is characterized by bands located between 1500–1300 cm\(^{-1}\), which correspond to the valence vibrations of the CH\(_3\) and CH\(_2\) groups [38]. The bands at 616 and 655 cm\(^{-1}\) corresponded to Zr–O and Zr–O–Zr vibrations, as well as to TiO\(_6\) structural units. There was also a wide band in the infrared spectrum of mixture A at 785 cm\(^{-1}\), which could have been related to the vibrations of the butoxy groups (Figure 5a). The spectrum in Figure 5b also revealed a peak at 1627 cm\(^{-1}\), which could be assigned to Zr(OCl)\(_2\)-8H\(_2\)O [39]. The 1100 and 1040 cm\(^{-1}\) bands were related to the fluctuations of terminal and bridge C–O bonds in the butoxy ligands [40]. It must be noted that the intensities of the peaks in the spectra of A and B mixtures (ranging from 600 to 1550 cm\(^{-1}\)) were different. Smaller intensities of the peaks in the B mixture in comparison to those in mixture A could be explained by a higher degree of hydrolysis (decreased number of non-hydrolyzed alkoxy groups) [30].

![Figure 4: Typical XRD spectrum of freshly prepared ZrO\(_2\)–TiO\(_2\) coating, treated at 500 °C (sample A5).](image)

![Figure 5: IR spectra of the dried precursor solutions A (a) and B (b).](image)
3.4. SEM Studies

The morphology of the samples was investigated by SEM analysis, while the surface topography was evaluated by atomic force microscopy. All of the coatings possessed the island-like surface structure typical of sol gel coatings, without any deep cracks. Figure 6 reveals the typical morphology of freshly prepared coatings, obtained from different ZrO$_2$ precursors.

![Typical SEM morphology of A4 (a), B4 (b), A5 (c) and B5 (d) fresh coatings.](image)

**Figure 6.** Typical SEM morphology of A4 (a), B4 (b), A5 (c) and B5 (d) fresh coatings.

3.5. AFM Studies

The AFM method was used for a more precise examination of the surface on the nanometric scale, and the obtained images gave additional information on the presence of visible corrosion damage, such as pores, surface irregularities, etc. Table 1 represents the $R_a$ values for all freshly prepared coatings and after immersing them in corrosive medium.

**Table 1.** Roughness values of the ZrO$_2$–TiO$_2$ coatings: fresh coatings and after immersing them in corrosive chloride media.

| Sample   | $R_q$ (nm) | $R_a$ (nm) |
|----------|------------|------------|
| A4 fresh | 31.0       | 23.2       |
| A4 after | 22.2       | 18.4       |
| B4 fresh | 12.8       | 10.1       |
| B4 after | 9.5        | 6.7        |
| A5 fresh | 49.0       | 35.7       |
| A5 after | 51.4       | 39.6       |
| B5 fresh | 15.2       | 11.3       |
| B5 after | 26.4       | 18.2       |
Figure 7 shows the topography of the coating A4 after 400 °C thermal treatment (Figure 7, left) and after conducting a corrosion test (Figure 7, right). It could be seen that the coating was dense, without any visible pores and having good adhesion. The roughness calculated by the AFM software program, $R_q$, was 31 nm ($R_a = 23.2$ nm). The surface roughness was also very close to the data for the sample (A4) before immersing it in the NaCl model corrosive medium. $R_q$ reached 22.2 nm, which was further evidence that the sample exhibited good anti-corrosion properties under the influence of NaCl for many hours. The freshly prepared coating after thermal treatment at 500 °C (A5) was relatively dense, possessing good adhesion (Figure 8). The roughness of this sample was higher than that of the A4 coatings treated at 400 °C (Table 1). The surface roughness after the corrosion attack did not change significantly, which could be regarded as a sign for excellent anti-corrosion properties of these samples.

![Figure 7. 3D topography of sample A4: fresh (left) and after corrosion attack (right).](image)

The composites of group B, synthesized using inorganic zirconium precursor and titanium butoxide (Figures 9 and 10, respectively), had a significantly lower roughness compared to those obtained using an organic Zr precursor, regardless of the temperature of the thermal treatment. Summarizing these data, it must be noted that after conducting of salt spray test, the roughness of the coatings increased slightly; the surface of all of the coatings was dense, showing an absence of any defects and any other signs of corrosion such as pits, cracks, etc. This result proves their excellent anticorrosion performance.
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Figure 8. 3D morphology of sample A5: fresh (left) and after corrosion attack (right).

Figure 9. 3D morphology of sample B4: fresh (left) and after corrosive attack (right).

Figure 10. 3D morphology of sample B5: fresh (left) and after corrosive attack (right).

3.6. XPS Investigations

The surface composition and chemical state of TiO2–ZrO2 layers were investigated by XPS. The analysis showed peaks of C1s, O1s, Zr3d and Ti2p on the surface of the films. The O1s peaks were broad and asymmetric, and they could be deconvoluted by a...
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3.7. Contact angle and NSS Measurements

3.7.1. Relationships between the Corrosion Stability and Hydrophobicity

Figure 12a represents the photographs of water drops on the coatings surface. All of the samples possessed a hydrophobic nature of the surface. The water contact angles had very similar values, as they were within a range varying from 82 to 90 [44]. It is well known that the hydrophobicity of a material surface is determined by both intrinsic chemical properties and surface microstructure. It was found that the hydrophobic nature of the surface often (as a rule) inhibits the corrosion process, by limiting the surface–corrosive species (water, halide ions, etc.) interaction. The experimental data on the dependence between the hydrophobicity and the corrosion properties, obtained by many research groups, have been contradictory. It has been proved that superhydrophobic material improves corrosion resistance [45]. On the other hand, several researchers have revealed the absence of a direct correlation between the high contact angle of water and better anti-corrosion protection [46]. Huang and co-authors [47] also found that superhydrophobic TiO$_2$ nanotubes possess low corrosion resistance.
Figure 12. (a) Photographs of the water drops on the surface of ZrO$_2$–TiO$_2$ coatings; (b) Effect of contact angle on the weight loss of the samples.

Figure 12b shows that the water contact angle value did not significantly influence the barrier properties (evaluated by Neutral Salt Spray corrosion tests); moreover, no clear correlation between the surface hydrophobicity and the barrier properties of the coatings could be observed. The coatings of ZrO$_2$–TiO$_2$, treated at 500 °C, prepared by both an organic and inorganic zirconium precursor exhibited better protective properties than those prepared at 400 °C i.e., zero weight loss after the corrosion attack.

3.7.2. Relationships between the Corrosion Stability and Surface Chemistry

Figure 13 represents surface chemical composition (evaluated by XPS analyses) as a function of the weight loss measurements. It is clearly visible that the oxygen to metal ratio (O/Ti + Zr) was not a definitive factor for better corrosion resistivity of the coatings. Furthermore, it could be seen that the hydroxyl group content on the surface influenced the corrosion-resistance properties. It was obvious that a sample with an O/OH ratio lower than three (A4) lost a considerable share of its weight after immersion into the...
corrosive medium, while the other three samples displayed zero weight loss. The available literature data on the influence of the surface stoichiometry of ZrO$_2$ films on their corrosion stability are insufficient. Concerning these effects, only one research group has mentioned something about the possible effect of the excess lattice oxygen content on the barrier properties of the CeO$_2$ sputtered films [44]. However, even they did not provide conclusive evidence of the extent and how the chemical composition of the surface affected their corrosion stability.

Figure 13. Correlation between weight loss and surface chemical composition, evaluated by XPS analyses.

3.8. Potentiodynamic Investigations

Figure 14 demonstrates the results obtained based on the potentiodynamic polarization curves of the investigated samples in the model corrosive medium of 3.5% NaCl solution. It was obvious that the values of the corrosion potential for the coatings in both groups were relatively similar (see Table 2 below).

Table 2. Electrochemical parameters according to the PD polarization curves.

| Sample | $E_{corr}$ (V) | $I_{corr}$ (A/cm$^2$) | $I_{pass}$ (A/cm$^2$) |
|--------|---------------|----------------------|----------------------|
| A4     | -700          | $7.0 \times 10^{-6}$  | $9.5 \times 10^{-5}$  |
| B4     | -674          | $2.5 \times 10^{-6}$  | $3.8 \times 10^{-5}$  |
| A5     | -685          | $3.8 \times 10^{-6}$  | $9.4 \times 10^{-5}$  |
| B5     | -675          | $4.1 \times 10^{-6}$  | $6.7 \times 10^{-5}$  |

The values of the corrosion current density and the average value of the current in the passive zones ($I_{pass}$) were measured approximately in the middle of the passive zone (at $\sim -300$ mV). It was obvious that the sample A4 manifested the highest $I_{corr}$ and $I_{pass}$ values. In the anodic zone of the polarization curves of all investigated samples, a delay in the current density values could be observed during the course after the corrosion potential. This was related to the appearance of passive zones in the potential interval between $-600$ and $-50$ mV, in which the value of the anodic current remained almost constant, despite the change in the potential. Generally, these zones are an indication of a slower rate of the anodic process of dissolution of the coatings under conditions of external polarization. Moreover, all the investigated coatings had passive zones, which confirms their good protective properties.
The values of the corrosion current density and the average value of the current in the passive zones (Ipass) were measured approximately in the middle of the passive zone despite the change in the potential. Generally, these zones are an indication of a slower –600 and –50 mV, in which the value of the anodic current remained almost constant, typically having a higher roughness value, ensures lower openness [49]. The openness of the grooves is characterized by the ratio w/d, where w is the width, and d is the depth of the grooves. A bigger w/d value (above some critical value) means smoother surface, and it is more difficult to micropit and to nucleate, and respectively, the corrosion rate is lower. As a result, the diffusion of the corrosive ions out of the formed grooves is limited; hence, they

4. Discussion

It could be generally concluded that samples B4, B5 and A5 were characterized by improved corrosion resistance upon external anodic polarization (lower corrosion and anodic current densities, respectively, as well as more positive corrosion potentials) compared to sample A4. On the basis of the results, obtained by potentiodynamic measurements (Figure 13 and Table 1), it can be concluded that the degrees of influence of the factors Ttr and the type of the zirconium precursor were different. In the cases of the samples A4 and B4 based on the PD curves, one could observe enhancement of the effect of the precursor in comparison with Ttr; the use of Zr butoxide led to a deterioration of the zone of passivation, while in the case of the samples heated at 500 °C, the influence of the precursor was minimized. Among the well-known factors which determine the corrosion stability of coatings are the amorphous structure, hydrophobicity and comparatively low roughness of the surface. It was seen that the surface morphology of the investigated layers also played an important role, bearing in mind the AFM images from Figures 6–9. The surfaces of the samples demonstrated different roughness (degree of surface inhomogeneity) after the corrosive treatment. If the surface was more even, then this was generally accepted as a sign of greater corrosion resistance, since it is well known that an additional potential difference (leading to a higher corrosion rate) can appear between the concaved and protruded zones on the surface. According to [48], the influence of the surface morphology, represented by the roughness, on the corrosion rate can be described by the electron work function (EWF). The obtained results demonstrated that the corrosion rate increased when the surface roughness was greater, while its surface EWF decreased. The roughness could decrease the average EWF, but it would increase the fluctuation of the local EWF, which could promote the formation of microelectrodes, leading to corrosion acceleration. Generally, it seems that it is easier for the electrons in the vicinity of a peak to escape, compared to those in a valley (concaved zone), so that the peak will corrode preferentially. It can be expected, based on these investigations, that a smoother surface will lead to better corrosion resistance of the investigated coating. The formation of a corrosion cell could be promoted by EWF fluctuations, thus leading to enhanced corrosion rate of a rough surface.

In addition, Zuo et al. have explained that the surface with deeper grooves, respectively having a higher roughness value, ensures lower openness [49]. The openness of the grooves is characterized by the ratio w/d, where w is the width, and d is the depth of the grooves. A bigger w/d value (above some critical value) means smoother surface, and it is more difficult to micropit and to nucleate, and respectively, the corrosion rate is lower. As a result, the diffusion of the corrosive ions out of the formed grooves is limited; hence, they

Figure 14. PD polarization curves in a model medium of 3.5 wt.% NaCl solution: A4 and B4 coatings (a); A5 and B5 coatings (b).
have a higher possibility to grow larger. Burstein et al. showed that the smoother surface of stainless steel is less capable of propagating metastable pits than the rougher one, mainly because the sites of pitting on the smoother surface are, on average, more open [50].

The data in the literature regarding the effect of the degree of crystallization of the oxide materials on their anticorrosion properties have been contradictory. Holgado et al. revealed that partially amorphous ZrO$_2$ films deposited on brass and SiO$_2$ were very effective in preventing the corrosion process [51]. Other research groups have found that fully amorphous samples possess a higher corrosion resistance than that of the partially crystallized samples [52,53]. In the crystalline materials, the active sites are the grain boundaries, which initiate the corrosion process. It is known that the amorphous materials are thermodynamically unstable, with a chemically homogeneous structure (without precipitates, segregates, etc.) and without defects (grain boundaries, twins, etc.). As a result, the amorphous structure can also effectively reduce the diffusion of the ionic species, thus increasing the corrosion resistance.

Among the well-known factors that determine the corrosion stability of the layers are amorphous structure, hydrophobicity and relatively low surface roughness. In our case, we found that there was another parameter connected with the chemistry of the surface which guaranteed enhanced corrosion stability, the O/OH ratio. For example, samples B4 and group A with an O/OH ratio above three had zero weight loss in the corrosion medium and lower corrosion current densities according to the PD measurements. In light of the experimental data, we can conclude that the presence of an amorphous dense structure having a hydrophobic nature and small content of hydroxyl groups is responsible for achieving the good corrosion stability of the ZrO$_2$–TiO$_2$ coatings, deposited on stainless steel. Keeping in mind this interesting fact, our future investigations will be directed towards a more detailed investigation of these effects.

5. Conclusions

The ZrO$_2$–TiO$_2$ nanocomposite-coated specimens showed a higher corrosion resistance in the NaCl solution, surpassing the performance of the pure oxide coatings. All of the samples possessed a dense amorphous structure, having a hydrophobic nature, which was preserved after corrosion tests. It was established that the samples, treated at 400 °C, upon using of zirconium butoxide, manifested a deterioration of the zone of passivity, while after $T_{tr} = 500$ °C, the effect of the Zr precursor was weakened. The good anticorrosion performance of the composites could have been due to the synergism between the amorphous structure, topography (smoothness) and hydrophobicity. It is interesting to note that in addition to the above listed factors, the surface chemical composition was also essential for the improved protective properties. The obtained coatings were suitable for films covering stainless steel used in biomedical and industrial applications, in order to extend the duration of its service life time.

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