

Investigation of anticorrosive behavior of zirconia-titanium coatings in NaCl medium

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Abstract: Sol gel TiO_2 - ZrO_2 composite films were dip coated on stainless steel substrates and treated at 300, 400 and 500°C. The morphology and surface features were examined by Scanning electron microscopy (SEM) and X ray photoelectron spectroscopy (XPS). X-ray diffraction analyses (XRD) was applied to investigate the phase composition. The corrosion resistances of the coatings were studied by evaluation of the weight loss in NaCl medium. According to XRD while the Zr-Ti composites are amorphous after treatment even at 500°C. The surfaces of the coatings possess typical island structure. The coatings, treated at 500°C exhibit higher corrosion resistance than the other two type of samples. This could be explained by the amorphous structure of the composites, which lowers ion and electron conduction, high hydrophobicity and lower oxygen content.

Keywords: BARRIER COATINGS, CORROSION RESISTANT COATING, PROTECTIVE PROPERTIES

1. Introduction

Corrosion is one of the serious problems in the industrial equipment, human life and health, which can causes degradation, failure, and serious accidents as well as many economical losses. There are several methods of corrosion control: inhibitors, cathodic protection and inorganic and hybrid coatings. One of the most effective methods for protecting the surface of metals and alloys against corrosion in aggressive acidic solutions is used the coating, which have excellent chemical stability, high hardness, adhesive strength, long-term and/or high-temperature corrosion resistance [1]. Zirconia coatings are known to effectively protect metals, due to their very low electronic conductance, wide band gap and possess good passivating surface with low anodic dissolution rate. [2] Zirconia is an interesting material since it offers high mechanical strength, temperature resistance and chemical stability. [3] The composites based on ZrO_2 and TiO_2 possess the excellent chemical and barrier properties of both individual oxides. El-Lateef et al. have shown that the introduction of Zr into TiO_2 are beneficial for the corrosion resistance of the composite coatings on carbon steel. [4]

The aim of this article is to prepare and investigate the protective properties against salty medium of composites ZrO_2 - TiO_2 deposited by sol gel method.

2. Experimental

The steel substrates were ultrasonically cleaned in ethanol and acetone. The zirconium precursor was solution of zirconium butoxide; $Zr(OC_4H_9)_4$ and Acetyl acetone (Ac) dissolved in 2-propanol and small quantity of acetic acid. After stirring for 1 h, 0.4 ml polyethylene glycol (PEG) Mw=400 was added. Titanium solution was prepared using titanium butoxide; $Ti(OC_4H_9)_4$ and Ac dissolved in 2-propanol. The resulting solution was mixed with the zirconium solution in atomic ratio Zr:Ti=1:1. Then the substrates were immersed and withdrawn at a speed of 30 mm/min. The deposits were dried in air first at 100°C and 300°C for 1 hour consecutively. The procedures were repeated 5 times, after that the samples were treated at 300, 400°C and 500°C and denoted as A3, A4 and A5 respectively. The phase compositions of the samples were studied by X-ray diffraction (XRD) with $CuK\alpha$ -radiation (Philips PW 1050 apparatus). A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films. 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 Analytical Ltd.) using achromatic AlK α radiation with a photon energy of 1486.6 eV and charge neutralisation 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. The AFM images

are calculated. It was evaluated the average roughness of the surface (Ra) and its standard deviation (Rq). Contact angle measurements were performed using a Ramé-Hart model 290 automated goniometer with DROPimage Advanced v2.4 (Succasunna, NJ, USA) at room temperature. 2-5 μ L droplets were deposited on the sample surface with a Ramé-Hart automatic dosing system. The corrosion resistance of the investigated samples and uncoated stainless steel (reference sample) estimated by weight loss were studied using salty corrosive solution of 3.5% NaCl at 25°C (EN ISO10289/2006). The temperature of the solution and the air temperature were controlled by calibrated thermometers. The mass weight loss was determined after 650 hours of corrosion attack. The potentiodynamic polarization curves are performed for characterization of the anodic behavior and evaluation of the corrosion properties of the multilayer coating systems at conditions of external polarization in the model test medium using a VersaStat 4 (PAR) unit. The investigations are 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.

3. Results and Discussion

In the XRD patterns of the composite films do not registered any crystalline phases, i.e. the films are X-ray amorphous structure. The morphology of the samples was investigated by SEM analysis as well as the surface topography by atomic force microscopy. In Figure 1 are shown the morphologies of the coatings before and after corrosion test (magnification 2500). It can be seen the typical island surface structure without deep cracks.

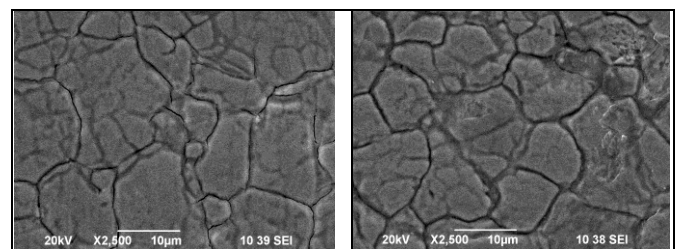
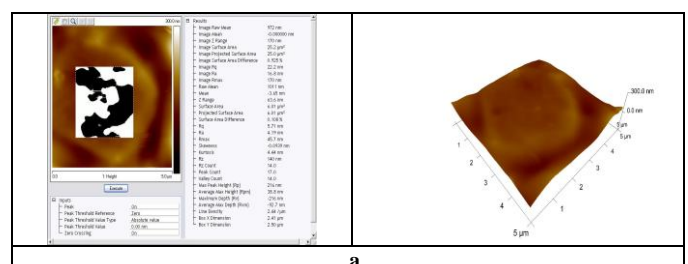


Fig. 1. Typical surface of coating A5 before (left) and after (right) corrosion test.



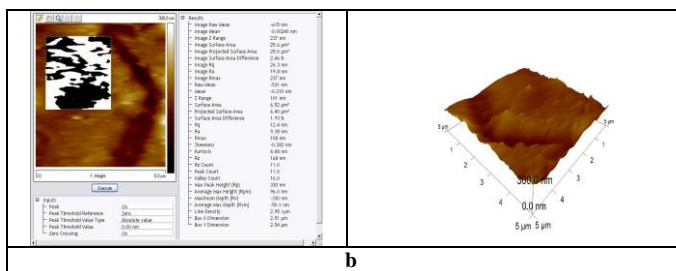


Fig 2. 2D u 3D morphology of coating A3 before (a) and after (b) corrosion attack.

Figure 2 shows the topography of the coating A3: it can be seen that the coating is dense, without visible pores and with good adhesion. The roughness calculated by the AFM software program Rq is 22 nm (Ra=16.8 nm). The surface roughness after corrosion attack is also close to the initial value: Rq is 26.3 nm (Ra=19.8 nm). After treatment of the coating at 500°C the coatings possess dense structure (Fig 3 a). Their roughness is higher than A3 coatings: Rq =48 nm (Ra=35.5 nm). The surface roughness values after immersing in a corrosive medium does not change significantly: Rq is 51.3 nm (Ra=39.6 nm), which confirms the excellent anti-corrosion properties of these samples.

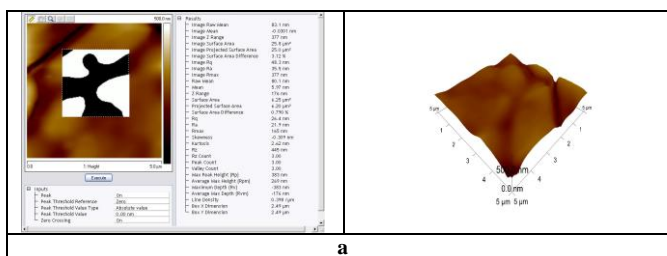


Fig 3. 2D u 3D morphology of coating A5 before (a) and after (b) corrosion attack.

The surface composition and chemical status of the TiO₂-ZrO₂ layers were examined by XPS analyzes. The chemical composition are presented on Table 1.

Table 1. The chemical composition.

| | Zr, at.% | Ti, at.% | O, at.% | O-OH groups, at.% | O/(Ti+Zr) |
|----|----------|----------|---------|-------------------|-----------|
| A3 | 14.0 | 13.8 | 72.2 | 26.5 | 2.60 |
| A4 | 14.0 | 13.8 | 72.2 | 23.2 | 2.60 |
| A5 | 14.8 | 14.7 | 70.6 | 20.8 | 2.39 |

The O1s spectra of the samples were shown in Fig. 4. The peaks of O1s are broad and asymmetric and can be deconvoluted by the Lorentzian-Gauss curve fitting into two components. The peak at ~ 529.7 eV can be assigned to the lattice oxygen in TiO₂ and ZrO₂. The second peaks at ~ 531.1 eV were attributed to the adsorbed hydroxyl groups. Ti2p spectra have peaks at ~ 458.3 eV for Ti2p_{3/2} / 2 and ~ 464.0 eV for Ti2p_{1/2}. The double separation between the 2p_{3/2} and 2p_{1/2} peaks of ~ 5.7 eV and the registered binding energies is characteristic of TiO₂. Zr3d_{5/2} peaks have a maximum at 182.0 eV, typical of the Zr⁴⁺ oxidation state.

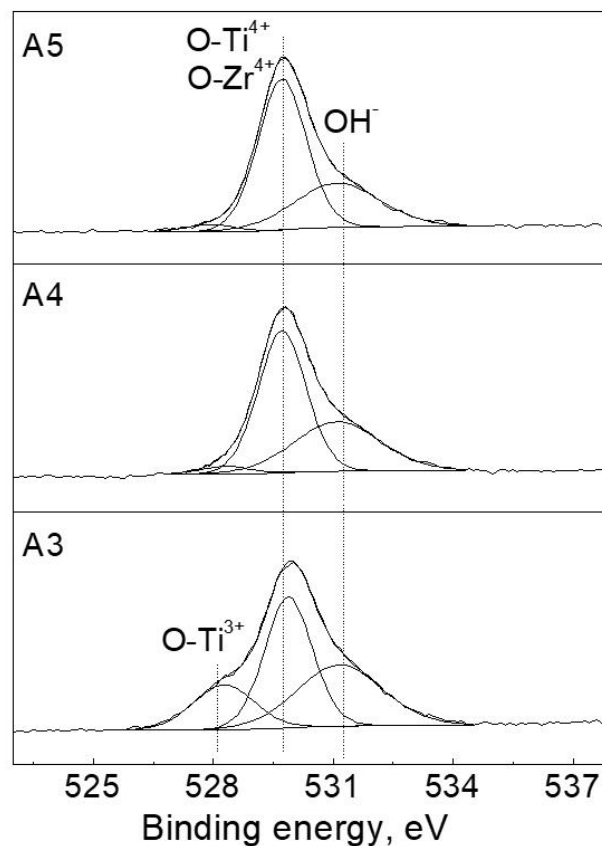


Fig 4. O1s spectra of the coatings after deconvolution.

The composite coatings possess relatively high hydrophobicity. The contact angles for all coatings are in the range 89° -95°.

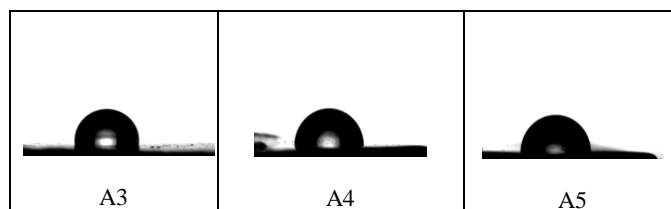


Fig 5. Optical images of water droplet on the TiO₂-ZrO₂ composite coatings.

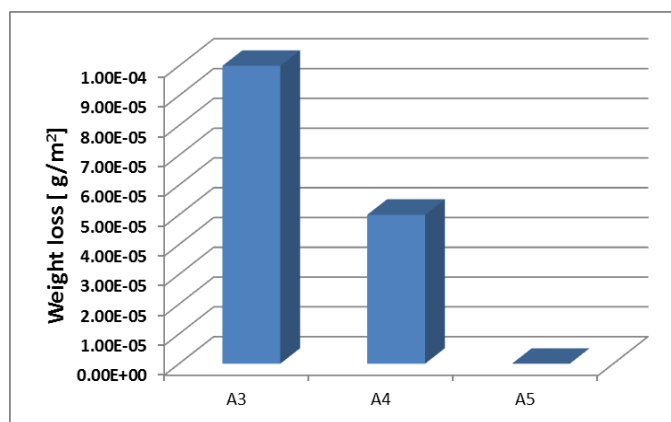


Fig 6. Weight loss of the coatings after immersion in NaCl medium.

The results of the corrosion test (Fig. 6) showed that the heat treatment temperature of has a significant effect on their corrosion resistance as assessed by weight loss. Zero weight loss registered for ZrO₂-TiO₂ coatings heated at 500°C.

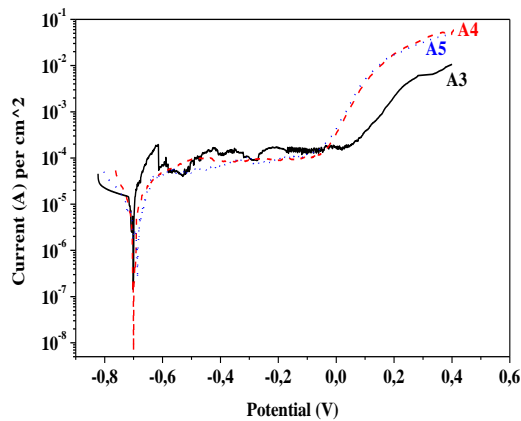


Fig 7. Potentiodynamic polarization curves in 3.5% NaCl solution of composite coatings.

The values of corrosion potential for the three types of coatings in this series are very close, i.e. -704 mV for A3, -700 mV for A4 and -685 mV for A5. (Fig. 7). The density of the corrosion current for the individual samples is as follows: for A3 - $1.4 \cdot 10^{-5}$ A/cm²; for A4 - $8.7 \cdot 10^{-6}$ A/cm²; for A5 - $4.5 \cdot 10^{-6}$ A/cm². In the anode zone there is a strong delay in the course of the polarization curves after the corrosion potential in all three samples, which is an indication of a slow anodic process of dissolution of the coatings in the conditions of external polarization. In all three curves passive zones in the range -600 mV to -50 mV are registered, where the velocity of the anode current does not depend on the potential. This section is followed by an increase of the anode current, most likely due to increased oxygen release.

Probably, amorphous, hydrophobic surface structure and lower lattice oxygen content ensure the good protective properties of the coatings treated at 500°C. First, the amorphous structure deteriorates their ion/electron conduction, thus improving the barrier properties [5], as the increased crystallization leads to deeper and more pronounced boundaries between individual grains, which accelerate the intercrystalline corrosion processes between the grains. Second, the existence of lower content of lattice oxygen of A5 coatings provides lower number of sites for hydrogen bonding with interfacial water thus increasing the hydrophobicity. In addition to these propositions, it could be supposed that the increased amount of carbon acts as corrosion inhibitor. According to Li et al. some carbon contaminations from organic precursor impede the mobility of species towards steel substrate [6].

4. Conclusions

A new composite titania-zirconia coatings heated at three different temperatures were successfully prepared by sol gel method. The corrosion resistances of the samples were examined in NaCl medium. The XRD analyses revealed that the coatings are amorphous. The protective layers possess relatively smooth and uniform surface structure. It was established that the treatment temperature of ZrO₂ influences significantly on their anti-corrosion behaviour. The increasing of temperature up to 500°C increases the corrosion resistance of the composites. The potentiodynamic curves have shown passive zones, followed by an increase of the anode current, most likely due to increased oxygen release. The good anticorrosion resistance of the TiO₂-ZrO₂ composites could be attributed to the amorphous structure, small grain size and low oxygen content.

Acknowledgements

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5. References

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