PREPARATION AND STUDY OF CORROSION STABILITY OF COMPOSITE COATINGS ON THE BASE OF ZrO_2 AND TiO_2

Chief Assist. Prof. Dr. St. Yordanov[1], Assoc. Prof. Dr. I. Stambolova[2], Assoc. Prof. Dr. V. Blaskov[2], Prof. Dr. L. Lakov[1], Assist. Prof. M. Shipochka[2], Chief Assist. Prof. Dr.V.Dyakova[1]
[1]Bulgarian Academy of Sciences, Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre "Acad. A. Balevski", Sofia, Bulgaria, e-mail: stancho14@abv.bg.
[2]Bulgarian Academy of Sciences, Institute of General and Inorganic Chemistry, Acad. G. Bonchev St., bl. 11, 1113 Sofia, Bulgaria

Abstract
Zirconium dioxide-titanium dioxide coatings were obtained by sol-gel method on stainless steel plates. The samples were treated at three *Zirconium dioxide-titanium dioxide coatings were obtained by sol-gel method on stainless steel plates. The samples were treated at three* *temperatures 300, 400 and 500^{o}C. The morphology and chemical surface composition were examined by Scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), while the phase composition was examined by X-ray diffraction analyses (XRD). The corrosion resistance was evaluated by weight loss measurements in NaCl medium. The coatings are possess relatively smooth surface with some microcracks. After corrosion test the coatings treated at 500^{o}C, keep their surface structure without visible signs of corrosion and thecorrosion tests revealed zero mass loss. The good protective properties of these coatings could be attributed to (i) amorphous structure, leading to deterioration of the ion and electron conduction of the films and (ii) probably increased density after the thermal treatment.*
Keywords: SOL-GEL, NANOSIZED FILMS, PROTECTIVE PROPERTIES, FILMS

1. Introduction

The stainless steels are widely used in various industrial applications because of their excellent corrosion resistance and their mechanical properties, but unfortunately in saline medium begins process of corrosion and as consequence the loss of the mechanical properties (especially the hardness) [1]. In order to improve the corrosion stability of the steels an excellent alternative for protecting is to coated the surface with oxide, carbide or oxynitride layer. The oxide coatings have attracted wide research interest because they can be provide high wear and corrosion resistance, thermal insulation etc of the steel. [2]. Titania and titania based composite coatings on metal surface can be used as catalysts, biomedical materials, solar cells and protective layers on metals surface to improve the corrosion resistance [3]. Zirconia (ZrO_2) is an important ceramic material for industry applications due to its wide band gap and thermal stability, the latter of which is attractive to be used as a barrier coating for stainless steel [4]. Currently, several techniques are commonly used to deposit ZrO_2 and ZrO_2 composite oxide coatings on steel surfaces: chemical such as sol–gel deposition [5], physical as: pulsed laser deposition (PLD) [6] chemical vapor deposition [7], magnetron sputtering technique [8]. Among them, the sol–gel method appears to be promising as it is low cost deposition method with capacity to yield coatings with a wide range of compositions on substrates with different size or geometry. Zirconia-titania compositions have gained use as a good thermal and corrosion protective barrier coating due to their properties as a combined material. Recently, Wang et al. have showed that the ZrO_2/TiO_2 coatings possesss superior corrosion resistance, cytocompatibility an antibacterial property and have potential in the fields of titanium alloy implants [9] The aim of this study is to prepare the composites ZrO_2-TiO_2 using organic Zr precursor and to investigate the effect of thermal treatment on their corrosion resistance in NaCl medium.

2. Experimental procedures

Zirconium solution A was prepared using zirconium butoxide; $Zr(OC_4H_9)_4$ and AcAc dissolved in 2-propanol and small quantity of acetic acid. Finally, polyethylene glycol (PEG) Mw=400 was added. The mixture was stirred for 2 hours. The steel substrates were ultrasonically cleaned in ethanol and acetone. Then the substrates were immersed and withdrawn at a speed of 30 mm/min. The procedures deposition drying at 300 ^{o}C were repeated 5 times, after that the samples were treated at 300^{o}C, 400 и 500 ^{o}C and denoted as A3 , A4 and A5, respectively.

The phase compositions of the samples were studied by X-ray diffraction (XRD) with CuKα-radiation (Philips PW 1050 apparatus). A scanning electron microscope (SEM) Philips 515 was used for morphology observations of the films. The surface topography was studied by means of Atomic Force microscope (AFM) (NanoScopeV system, Bruker Inc.) operating in tapping mode in air. The scanning rate was set at 1 Hz. Subsequently, all the images were flattened by means of the Nanoscope software. 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.) using achromatic AlKα 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 and Zr3d photoelectron peaks. 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 calculation of the corrosion rates K of in salt medium [g/m^{2}h]) was performed by determining the mass loss coefficient Δm (g) for each test period. In order not to disturb the integrity of the test coating, the samples were washed several times with distilled water and dried before weighing.

3. Results and discussion

The XRD patterns of the samples were not revealed any peaks of crystalline ZrO_2, so the structures are amorphous. It have been established that the structure of the ZrO_2-TiO_2 sol gel membranes is still in amorphous phase up to 500°C and that the crystallization temperature of the mixed TiO_2/ZrO_2 powder has been significantly increased compared with the pure oxides. In addition Aust et al. have studied the crystallization behavior of the composite powders ZrO_2-TiO_2 and have proved that up to 600^{o}C the composites are still amorphous [10]. The amorphous structure of the composites suggests the high thermal stability.
The surface composition and chemical state of the TiO_2 - ZrO_2 layers were investigated by XPS. The XPS analysis shows peaks of C1s, O1s, Zr3d and Ti2p on the surface of the films. The O1s peaks are wide and asymmetric and two oxygen states are observed. The first ones at ~529.8 eV are assigned to lattice oxygen in TiO_2 and ZrO_2. The second peaks at ~531.6 eV are attributed to adsorbed hydroxyl

groups. The Ti2p spectra have a peaks at ~458.3 eV for $Ti2p_{3/2}$ and ~464.0 eV for $Ti2p_{1/2}$. The doublet separation between the $2p_{3/2}$ and $2p_{1/2}$ peaks of ~5.7 eV and the registered binding energies are characteristic of TiO_2. The $Zr3d_{5/2}$ peaks have a maximum at 181.9 eV, typical for Zr^{4+} oxidation state (Fig. 1). In precursor solution quantity of TiO_2 and ZrO_2 is 50 mol %. XPS analyzes show that the TiO_2:ZrO_2 atomic ratio is 1:1 on the surface of the films, obtained by Zr $(OBu)_4$, which corresponds well to the ration in the precursor solution.

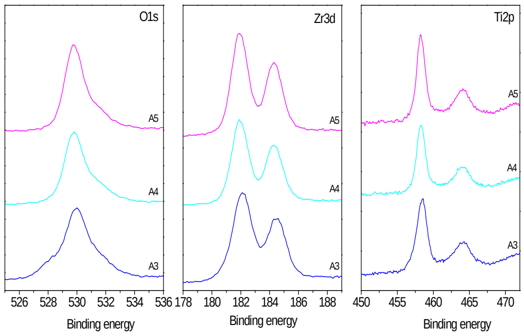

***Fig. 1.** O1s, Zr3d, Ti2p core level spectra of the coatings*

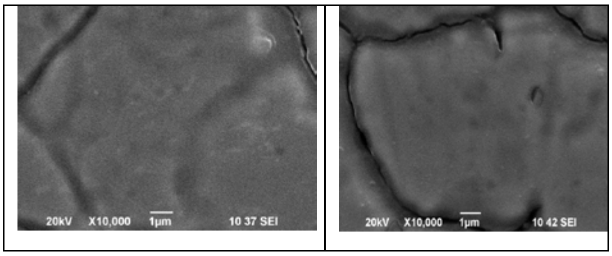

Fig. 2. *Morphology of fresh coatings A3 (left) and after corrosion (right)*

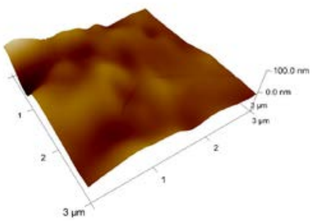

***Fig 3**. AFM image (3D) of surface of fresh coating A3*

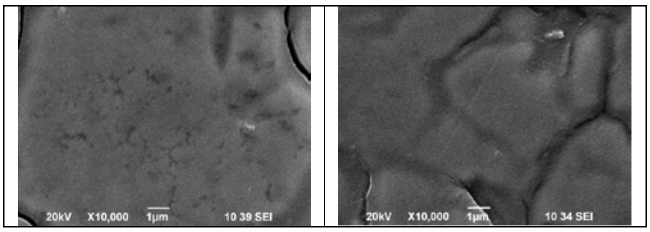

***Fig 4**. Morphology of fresh coatings A5 (left) and after corrosion (right)*

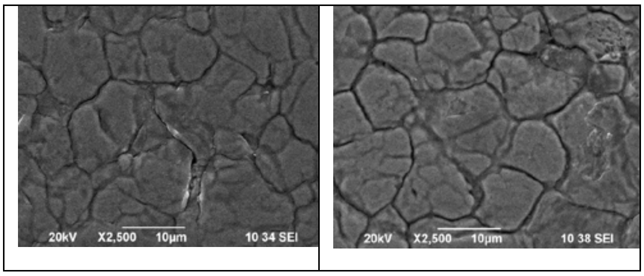

***Fig 5**. Morphology of coatings A3 (left) and A5 (right) after corrosion (right)*

The coatings, treated at 300°C have island surface morphology with shallow microcracks (Fig 2 and 3). The average roughness of A3 fresh sample, calculated by the AFM software program R_a is10 nm). After corrosion test the surface of A3 exhibits more profound signs of the acid attack. The samples A5 exhibit similar surface, bur longer cracks are observable. (Fig 4). This can be attributed to the intrinsic stress resulting from the mismatch between the thermal expansion coefficient of the substrate and the coating (α_{ZrO2} ~ 12.10^{-6} /°C, α_{steel} ~16.10^{-6} /°C). The main surface features do not change significantly after the immersion in salt medium and keep its island structure. Figure 5 reveals the main morphology features of the samples treated at 300 and 500°C after the corrosion attack. It can to be noted that the samples treated at higher annealing temperatures possess shallow borders between the surface islands, while the lower temperatures of treatment induces more pronounced and deeper cracks.

The corrosion test by weight loss method in Neutral Salt Spray Chamber showed that composite coatings ZrO_2 –TiO_2 treated at 500°C have higher corrosion resistance (corrosion rate is zero) than the coatings, treated at lower temperatures. (Fig.6). This result probably is due to (a) the amorphous structure of the investigated samples (as can be seen from the XRD data). It was proved that the presence of amorphous structure of TiO_2–CeO_2 composite deteriorates the ion and electron conduction of the films, which in turn improves the barrier properties [10]; (b) the increased treatment temperature leads to densification and consequently increased coatings hardness. These two suppositions may be the reason for the better protective properties of the investigated system on the base of ZrO_2 and TiO_2 coatings..

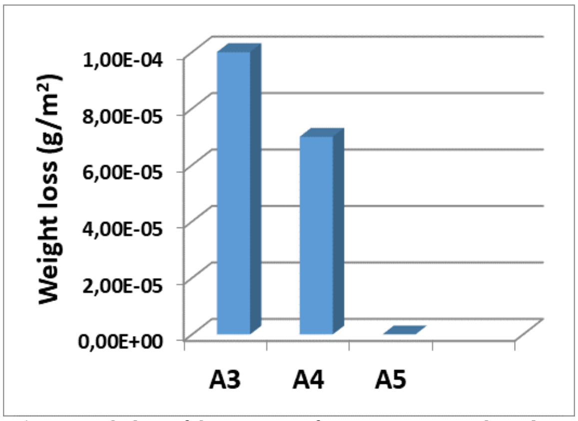

***Fig 6**. Weight loss of the coatings after immersion in salt medium*

4.Conclusions

Zirconia-titania amorphous films have been prepared by sol-gel technology and were studied as protective barriers against corrosion. The samples possess relatively dense island structure with shallow microcracks. The XPS data revealed that the $Zr3d_{5/2}$ peaks corresponds to Zr^{4+} oxidation state. After corrosion test the surface of coatings, treated at 300°C exhibits more profound signs of corrosion, than those treated at 400 and 500°C. The coatings treated at higher temperatures (500°C) exhibited the best corrosion protective properties (corrosion rate is zero), than those treated at lower temperatures. This could be explained by the amorphous structure and probably higher density of the composites

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