Application of ZrO₂ and ZrO₂-TiO₂ Coatings as Corrosion Barriers: Surface Composition and Structure

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Abstract

Two types of zirconium oxide sol gel coatings: pure ZrO_2 and ZrO_2/TiO_2 composites were deposited by sol-gel method on stainless steel substrates. 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 the ZrO_2 coatings treated at 400ºC and 500ºC crystalized in cubic phase, while the Zr-Ti composites are amorphous after treatment at these temperatures. The surfaces of ZrO_2/TiO_2 coatings are smoother than those of ZrO_2 films. The composite coatings deposited on stainless steel have zero weight loss in corrosive medium, while ZrO_2 coatings exhibited lower corrosion resistance. This could be explained by the amorphous structure of the composites, which deteriorates the ion and electron conduction of the films due to the absence of grain boundaries.

Keywords: corrosion resistances, sol-gel technology, zirconia and zirconia-titania films

1. Introduction

The corrosion processes can damage many metal constructions such as: bridges, automobiles, airplanes, industrial plants, petrochemical, desalination, pharmaceutical, etc. which leads to a decrease in their efficiency and loss of useful or productive life. Corrosion prevention is performed through different techniques, and choosing the right one should be done while optimising between process cost, process performance, and corrosion effects.

Coating is the most widely used method for preventing corrosion. The nanocoatings possess improved thermal, mechanical, physical, chemical, magnetic, electronic, and optical properties [1]. The fine sizes of oxide nanocoatings form a uniform physical barrier on the surface of the material and could be successfully used as corrosion barriers. For this purpose ZrO_2, TiO_2, Al_2O_3, SiO_2 and their composites are the most effective protective materials against corrosion. The system ZrO_2-TiO_2 is very promising due to the interesting physicochemical properties of the individual oxides and was investigated in different areas. It was revealed that the mixed titania-zirconia particles prepared via UV (Ultraviolet rays)-induced crosslinking polymerization possess high refractive index, high transparency, good thermal stability and mechanical properties [2]. Srivastava et al. have successfuly applied titania–zirconia nanocomposite as urea detectors [3]. The addition of ZrO_2 into TiO_2 leads to improved photocatalytic activity as a result of decreased band gap and recombination rate. [4]. ZrO_2/TiO_2 porous coatings doped with zinc (Zn-ZrO_2/TiO_2) were prepared on titanium alloy. The biological experiments indicated that the coatings exhibit excellent antibacterial properties,

favorable cytocompatibilit and the corrosion resistance in the simulated body fluids [5]. Al Lateef et al. have prepared anticorrosive ZrO_2–TiO_2 nanocomposite coatings with different ZrO_2 loading for carbon steel. The high protection efficiency of composite coatings have explained by the mutual influence of TiO_2 and ZrO_2 films [6]. The aim of this article is deposition and investigation of anticorrosion properties of ZrO_2 and ZrO_2/TiO_2 composite coatings on stainless steel.

2. Experiment

2.1. Coatings preparation

The zirconium precursor was 0.25M ethanol solution of $ZrOCl_2.8H_2O$, (p.a) with small quantity of nitric acid, acetylacetone as complexing agent and 0.4 ml polyethylene glycol (PEG) Mw=400. The steel substrates were ultrasonically cleaned in ethanol and acetone. Then the substrateswere immersed and withdrawn at a speed of 30 mm/min. Then, the samples are 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 400ºC и 500 ºC and denoted as Z1 и Z2, respectively. Titanium solution was prepared using titanium butoxide; $Ti(OC_4H_9)_4$ and AcAc dissolved in 2-propanol. The resulting solution was mixed with zirconium solution in atomic ratio Zr:Ti=1:1. Then the deposition-drying procedures and final treatment followed the scheme described deposition of pure ZrO_2 coatings. The samples were treated at 400ºC и 500 ºC and denoted as ZT1 and ZT2, respectively.

2.2. Sample characterization and estimation of the anticorrosion properties

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. 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, Ti2p 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.

3. Results and Discussion

X-ray diffraction revealed a formation of ZrO_2 cubic crystallographic phase after thermal treatment of zirconia Z1 coatings (Fig.1). The patterns of the samples ZT1 and ZT2 were not revealed any peaks of crystalline ZrO_2, so the structures are amorphous. Similar results were presented by Guo et al. [7]. This research group have established that the structure of the TiO_2/ZrO_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. The amorphous structure of the composites suggests the high thermal stability.
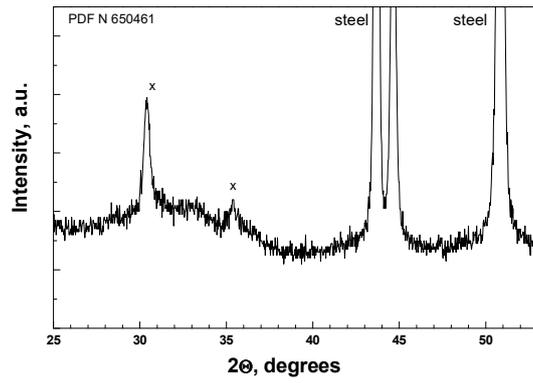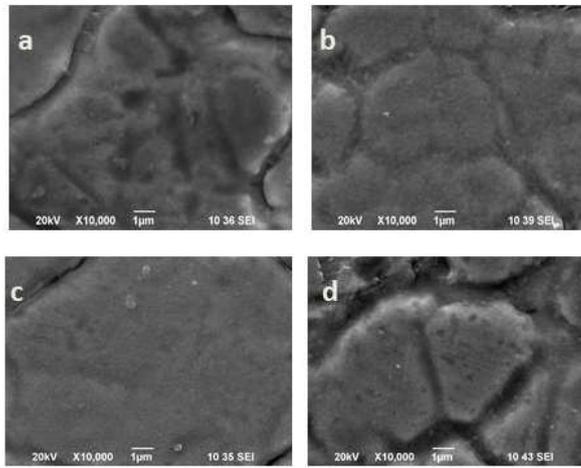
Fig.1 XRD pattern of ZrO2 (Z1) sample

Fig 2 Morphology of fresh coatings Z1(a), Z2 (b) and after corrosion Z1 (c); Z2(d)
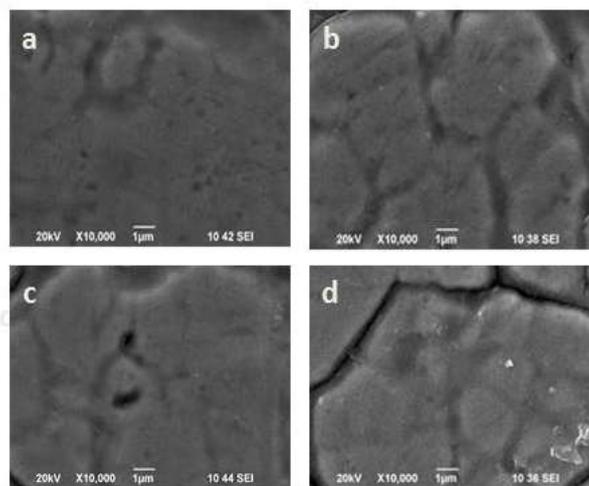

Fig. 3 Morphology of fresh coatings ZT1(a), ZT2 (b) and after corrosion ZT1 (c); ZT2(d)

The SEM photographs of Z1 and Z2 fresh samples are presented in Fig. 2. The coatings, annealed at 400ºC and 500ºC have island surface morphology with shallow microcracks. After corrosion test the surface of Z1 remains its characteristics, while the morphology of Z2 exhibits some visible signs of the acid attack: pits, cracks etc. The samples ZT1 and ZT2 exhibit smoother surface, than Z1 and Z2. The main surface features do not change significantly after the immersion in salt medium.
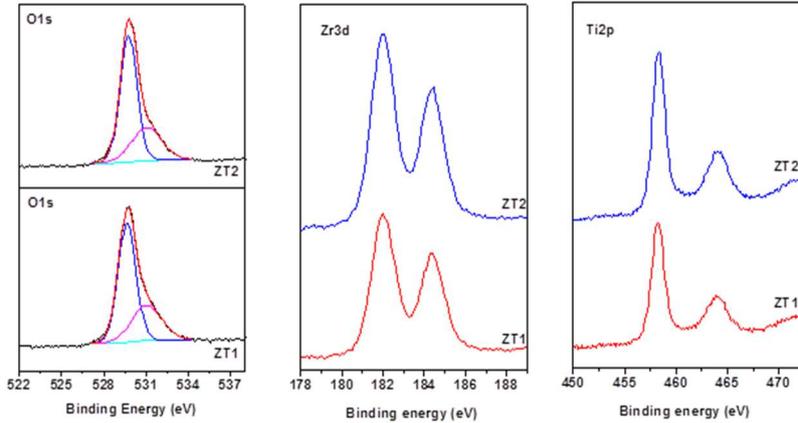

Fig. 4 Deconvolution of O1s; Zr3d and Ti2p core level spectra of fresh composites ZT1 and ZT2
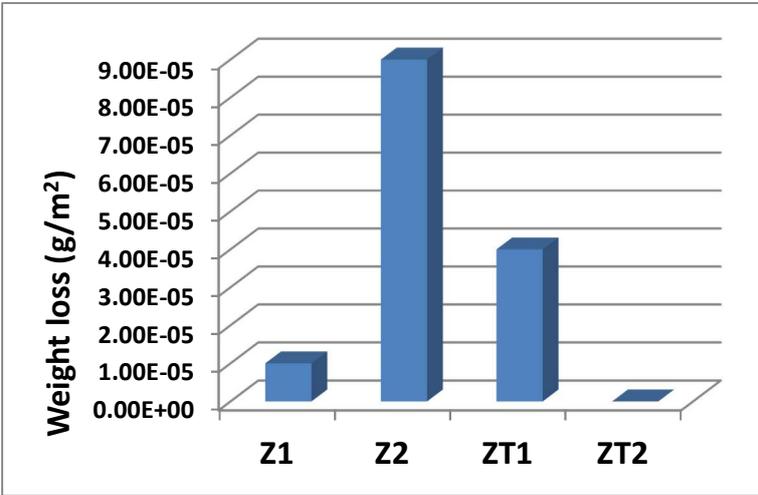

Fig 5. Weight loss of the samples after corrosion attack

The XPS analyses were performed and show peaks of C1s, O1s, Zr3d and Ti2p on the surface of the films (Fig. 4). The O1s peaks are wide and asymmetric and could be deconvoluted by Lorentzian–Gaussian curve fitting into two components. The first ones at ~529.7 eV are assigned to lattice oxygen in TiO_2 and ZrO_2. The second peaks at ~531.1 eV are attributed to adsorbed hydroxyl groups. The Ti2p spectra have a peaks at ~458.3 eV for Ti2p3/2 and ~464.0 eV for Ti2p1/2. The doublet separation between the 2p3/2 and 2p1/2 peaks of ~5.7 eV and the registered binding energies are characteristic of TiO_2 (Fig. 4). The Zr3d5/2 peaks have a maximum at 182.0 eV, typical for Zr4+ oxidation state. The corrosion test by weight loss method in Neutral Salt Spray Chamber showed that pure ZrO_2 definitely have lower corrosion

resistance than the ZrO_2/TiO_2 composite coatings. (Fig. 4). This result probably is due to the more pronounced crystallization of of the samples Z1/Z2 (as can be seen from the Fig. 1). It could be supposed that the increased crystallization leads to deeper and more pronounced boundaries between individual grains, which accelerate the intercrystalline corrosion processes between the grains. It was established for TiO_2–CeO_2 composite films that the amorphous structure deteriorates their ion/electron conduction, thus improving the barrier properties [8].

Conclusions

Zirconia and zirconia-titania films have been prepared by sol-gel technology and were studied as protective barriers against corrosion. Pure zirconia films exhibit cubic phase, while the composites are amorphous. The samples possess relatively dense structure with shallow microcracks. The pure zirconia coatings treated at higher temperatures (500ºC) manifested lower corrosion stability than those treated at 400ºC. It was established that the ZT1 and ZT2 composite samples, treated at 400ºC and 500ºC manifested better stability to corrosion attack than Z1 and Z2 probably due to their amorphous structure.

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