EFFECT OF TREATMENT TEMPERATURE OF TiO_2/SiO_2 AND ZrO_2/SiO_2 COATINGS ON THEIR CORROSION STABILITY

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Abstract *Titanium dioxide coatings and zirconium dioxide were deposited on SiO_2 underlayers by sol-gel method on stainless steel plates. The samples were treated at two different temperatures (500 and 700^{o}C) in air. The morphology was examined by means of Scanning electron microscopy (SEM) and the phase composition by X-ray diffraction analyses. The corrosion resistance of the coatings were examined by evaluation of the weight loss in NaCl medium. The TiO_2/SiO_2 coatings possess relatively smooth surface with some crystallites on the surface, while ZrO_2/SiO_2 coatings are not so smooth. After treatment at higher temperature the ZrO_2/SiO_2 coatings become rougher. The weight loss measurement have proved that the TiO_2/SiO_2 coatings exhibit higher corrosion resistance in comparison to ZrO_2/SiO_2 coatings. The TiO_2/SiO_2 coatings, treated at 500^{o}C after the corrosion test retain their characteristic grain structure without any cracks and other defects. Similar is the structure of these coatings, treated at 700^{o}C. The better protective properties of TiO_2/SiO_2 could be attributed to their amorphous dense structure.*

Keywords**: SOL-GEL, MULTILAYERS, NANOSIZED FILMS, BARRIER PROPERTIES, FILMS**

1.Introduction

Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, which has many serious economic, health, safety etc consequences. There are several methods of corrosion control: inhibitors, cathodic protection and applying of coatings. Coatings for corrosion protection can be divided into two broad groups - metallic and nonmetallic (organic and inorganic). [1,2] Recently, the inorganic oxide coatings are increasingly used for range of industrial applications to provide wear and erosion resistance, thermal insulation and corrosion protection [3]. Among them, ZrO_2 coatings have good chemical and thermal stability, high strength, high dielectric constant etc., which make them suitable for anticorrosiion coating for steels protection [4]. Titania coatings are also widely used as anticorrosion coatings on stainless steel [5-7]. The physical and chemical properties of the both ZrO_2 and TiO_2 films strongly depend on the deposition method and the corresponding heat treatment process, especially the temperature of thermal teatment [8]. Multilayer coatings have recently been increasingly used as anticorrosive coatings because they provide better protective properties compared to monolayer coatings. [9] The multilayer configuration of the two types of oxides applied to each other has the combined effect of their advantages, and the surface layer to protect the parent metal should have increased corrosion resistance. The aim of this article is to study the the effect of the heating temperature of ZrO_2 and TiO_2 nanosized coatings, deposited over silica sol gel layers to their corrosion resistance.

2. Experimental

The silica underlayers were prepared from tetraethoxyl silane (TEOS) dissolved in a mixture of ethanol, water and hydrochloric acid as a catalyst. The molar ratio H_2O: TEOS is 3.7. The solution undergoes aging for 7 days. Stainless steel AISI 316 7.5x 2.5 cm were cleaned ultrasonically in ethanol and acetone, after taht were immersed in the solution and withdrawn at a constant rate of 3 cm / min and then dried at 60°C and at 90°C and finally at 300°C. These steps are repeated two times. In ZrO_2/SiO_2 (SZ) samples were deposited three ZrO_2 layers over SiO2 layers, using $ZrOCl_2$.8H2O with a acetylacetone and then dried sequentially at 300°C. The dipping-drying steps were repeated 3 times, finally was carried out final treatment at 500°C or 700^{o}C (sample code SZ5 and SZ7, respectively). The same procedure was applied for the preparation of TiO_2 /SiO_2 samples with codes ST5 and ST7. The TiO_2 coatings were deposited from precursor titanium isopropoxide Ti $(OC_3H_7)_4$ (98%), dissolved in a mixture of ethanol and butanol . 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 chemical corrosion resistance of the investigated samples and uncoated stainless steel (reference sample) were studied by immersion in salty corrosive solution of 3.5% NaCl at 25°C (EN ISO10289/2006) for 200 hours .The temperature of solution and the air temperature were controlled by calibrated thermometers.

3. Results and discussion

The figure 1-a indicates the presence of ortophombic crystallographic phase of ZrO_2 and SiO_2 phase in sample SZ5 with crytallites sizes 44 and 75 nm , respectively. After heating at 700^{o}C the sample SZ7 crystallizes in cubic ZrO_2 phase with very fine crystallites (9 nm) (Fig 1b). The X-ray diffraction patterns of sample ST5 heated at 500^{o}C do not indicate the presence of a crystalline phase of TiO_2, i.e. the sample has amorphous structure (Fig 1-c) During the isotermical heating at 700^{o}C both phases are formed: nanocrystalline anatase phase TiO_2 phase and SiO_2 phase. The same result was obtained from Cheng and co-authors for sol gel SiO_2 doped titanium dioxide films [10]. They have proved that the peaks intensity of the anatase phase is weakening with an increase in silica concentration and the films doped with 20% SiO_2 is amorphous. Another group of researchers also showed that the introduction of SiO_2 into TiO_2 nanoparticles suppress the crystallization of the anatase phase [11].

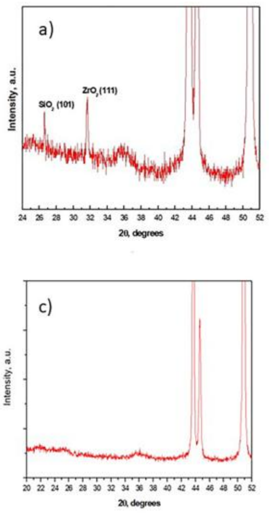

Fig. 1 *XRD patterns of the TiO_2 and ZrO_2 coatings on silica underlayers: SZ5 (a), SZ7 (b), ST5 (c) and ST7 (d)*

The morphology of multi-layered ZrO_2 and TiO_2 coatings on silicon dioxide: freshly prepared and after the corrosion test is presented on figures 2 and 3. The coatings SiO_2/ZrO_2 are relatively thick with the presence of nanosized pores (Fig 2). The surface of ST sample is relatively dense with a few surface nanocrystals of different sizes.(Figure 3a) There are no visible cracks and pores. After thermal treatment at 700°C more numerous larger superficial nanocrystals are observable (Figure 3b). After the corrosion test the roughness of titania coatings deposited on SiO_2 treated at lower temperature increases slightly without showing any effects of corrosion such as cracks and other defects (Figure 3c). The corrosive attack deteriorates significantly the surface of the samples, treated at 700°C (not shown here).

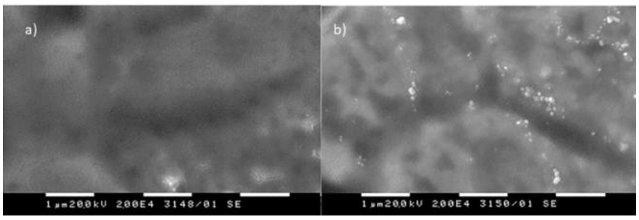

Fig. 2 *Morphology of the SZ5 (a) and SZ7 coatings (b)*

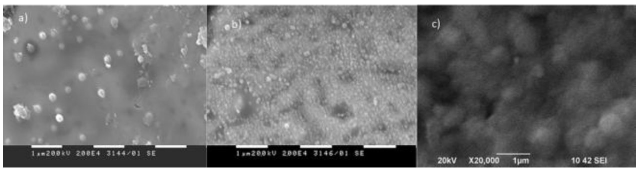

Fig. 3 *Morphology of ST5 (a) and ST7 coatings (b) and after corrosion test : ST5 (c)*

As it can be proved by evaluation of mass of the samples after immersion in salime medium, TiO_2 on SiO_2 multilayers exhibit improved corrosion resistance in comparison with those of the ZrO_2/SiO_2. The best barrier properties were shown by TiO_2/SiO_2 underlayers, heated at 500°C. Zero weight loss was registered after 200 hours of corrosion test for these coatings. The TiO_2/SiO_2 coatings treated at higher temperature have shown sligtly weaker protective properties. Increased temperature of treatment of these ZrO_2/SiO_2 samples lead to strong inreasement of corrosion rate.

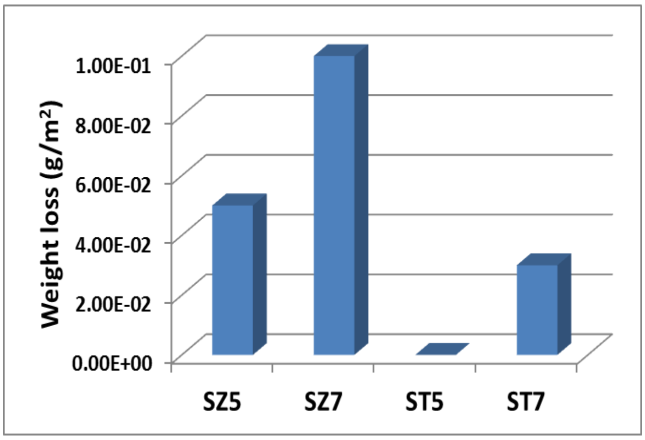

Fig. 4 *Weight loss of the multilayer samples ZrO2/ SiO_2 and TiO2/ SiO, treated at two different temperatures*

It was established by other research group that the presence of amorphous structure of TiO_2–SiO_2 composite deteriorates the ion and electron conduction of the films, thus acting positively on the corrosion protection [12]. The relatively dense, amorphous structure of the samples TiO_2 /SiO_2, may be reason for their better protective properties than those of the ZrO_2/SiO_2 multilayers.

4. Conclusions

Coatings, consisting of TiO_2 and ZrO_2 deposited over SiO_2 underlayers were obtained by dipping technique. The titania coatings on silica underlayer are relatively smooth with many crystallites on the surface,while the ZrO_2/ SiO_2 coatings are rougher . The TiO_2 coatings on SiO_2 treated at lower temperature manifested the higher corrosion resistance than that of ZrO_2 samples, which have been proved from the weight loss test in NaCl medium and the morphology studies. The increasing of the treatment temperature deteriorates the protection properties of the both types of coatings. The better protective properties of TiO_2/SiO_2, heated at 500°C, could be attributed to their amorphous structure and relatively dense surface. The obtained new multilayer structures are promising with the view to increase the corrosion resistance of the steel and this fact gives us the reason to extend the scope of the experiments.

5. Acknowledgements

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