Atomic force microscopy /AFM/ study of the surface morphology of TiO_2 featuring with Sm_2O_3 films obtained by the sol-gel method

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***Abstract*:** *In this paper we present the results of atomic force microscopy (AFM) characterization of the surface morphology of the nanostructured titanium oxide films featuring with Sm_2O_3 by the sol-gel method in order to increase the corrosion resistance of stainless steel. Two types of titanium precursors were applied - titanium (IV) isopropoxide $Ti[OCH(CH_3)_2]_4$ and titanium(IV) butoxide $Ti(OCH_2CH_2CH_2CH_3)_4$.*

***Keywords**: AFM, TIO_2 FILMS, Sm_2O_3, SOL-GEL METHOD*

1. Introduction

Atomic force microscopy (AFM) was used to study the influence of thermal treatments on the structural and textural properties of the sol-gel TiO_2 films obtained from $Ti(OC_3H_7)_4$. X-ray diffraction (XRD), ellipsometric and porosity measurements have also been made. The TiO_2 sol-gel films were homogeneous, transparent and amorphous. Heat treatments in the 400–600°C range indicate that the films have a strong tendency to crystallization. The high initial homogeneity of the TiO_2 films was preserved during the crystallization process. AFM shows that the thermally treated films exhibit uniform, monodispersed crystals [1].

The chemistry of the sol-gel process based on hydroxylation and condensation of molecular precursors has been extensively studied for silica. Transition metal alkoxides appear to be much more reactive than silicon alkoxides. This is due to the lower electronegativity of the transition metals compared with silicon and the ability of transition metal atoms to exhibit several coordination states [2, 3]. Among the transition metal alkoxides, those of titanium have been systematically studied both from experimental [4] and theoretical [2] points of view. In the literature are presented the results of Atomic Force Microscopy characterization of the surface morphology of the L-CVD SnO_2 thin films prepared by L-CVD technology and studied after exposure to air, dry air oxidation, and ion beam profiling. These experiments showed that the L-CVD SnO_2 thin films exhibit a very high quality surface morphology, what can be useful for solar cells and gas sensors application [5].

2. Experimental

In this study, nanosized TiO_2 coatings donated with samarium were obtained by the sol-gel method to increase the corrosion resistance of 316L steel. Two organic titanium precursors were used to prepare the solution for TiO_2 deposition donated with samarium: Titanium Isopropoxide (TTIP) and Titanium Butoxide. Acetylacetone (AcAc) was used as a stabilizing agent.

Titanium isopropoxide (TTIP); titanium butoxide and AcAc were dissolved in 2-propanol. The resulting solution is clear and orange, which is typical for the formation of a chelated complex. After stirring vigorously at room temperature, a mixed solution of distilled water and i-propanol (iPrOH) was added drop wise to the above solution with stirring. The molar ratio of the components is TTIP: iPrOH: H_2O: AcAc = 1:30:1:1. The solution of the Titanium butoxide was prepared by the same method.

A solution of Sm_2O_3 was prepared by dissolving in 2 M nitric acid and isopropanol to a final concentration of 0.1 M. The calculated amount of samarium solution is added to the titanium solution:

– Sample Sm 1 was prepared from a sol containing 0.5 at. % Sm in titanium isopropoxide solution;
– Sample Sam 2 was prepared from a sol containing 1 at. % Sm in titanium isopropoxide solution;
– Sample Sm 3 was obtained from a sol containing 0.5 at. % Sm in titanium butoxide solution;
– Sample Sm 4 was obtained from sol containing 1 at. % Sm in titanium butoxide solution.

The prepared samples from a sol containing different percentage of Sm in titanium isopropoxide solution or in titanium butoxide solution were studied and characterized by Atomic force microscopy (AFM). The obtained images are presented in the work.

Atomic force microscopy (AFM) is a modern method that is widely used in the field of nanotechnology for the study of surface structure and topography of various samples. In the study with an atomic force microscope, high precision and resolution in the nanometric scale is achieved.

AFM imaging was performed on the NanoScope V system (Bruker Ltd, Germany) operating in tapping mode in air at a room temperature. We used silicon cantilevers (Tap 300Al-G, Budget Sensors, Innovative solutions Ltd. Bulgaria) with 30 nm thick aluminum reflex coatings. According to the producer's specifications the cantilever spring constant and the resonance frequency are in the range of 1.5 to 15 N/m and 150 ± 75 kHz, respectively. The radius of tip curvature was less than 10 nm. The scanning rate was set at 1 Hz and the images were taken in highest possible resolution mode of the AFM, 512 × 512 pixels in JPEG format. The NanoScope software was used for the section analysis and roughness of the all images.

X-ray diffractometer with a Bragg-Brentano focusing system was used. The samples were studied at room temperature with Cu-Kα radiation (monochromatic radiation with a wavelength λ = 154178Å) in the range of $20^o < 2\theta < 65^o$, in steps of 0.04 2θ for 10 seconds. A graphite monochromator was used for better peak resolution (better signal-to-noise ratio).

3. Results and Discussion

The obtained results for the samples from the Sm series show very good protective properties of the applied sol-gel coatings. For sample Sm 2 after 50 hours of cyclic testing, the corrosion test showed little corrosion. As after 100 h of cyclic tests in sample Sm 3 no mass loss was reported and accordingly the corrosion rate is zero. This behavior can be explained by the presence of corrosion products in the pore volume, which leads to diffusion limitations - a barrier effect and slowing down the corrosion process.

3.1 Characterization of the measured surface of the samples Sm 1, Sm 2, Sm 3, and Sm 4 by Atomic force microscope

The topography of the samples Sm 1, Sm 2, Sm 3 and Sm 4 was measured using an atomic force microscope with a surface scan area - 5 µm, presented in Fig.1 and Fig.2. An analysis of the surface was made as well as an assessment of the roughness of the different coatings: - TiO_2-deposited coatings donated with different percentages of Sm_2O_3 in titanium isopropoxide solution (Sm 1 and Sm 2), as well as TiO_2-deposited coatings donated with different percentages of Sm_2O_3 in titanium tetrabutoxide solution (Sm 3 and Sm 4). The morphology and roughness of the coatings were compared.

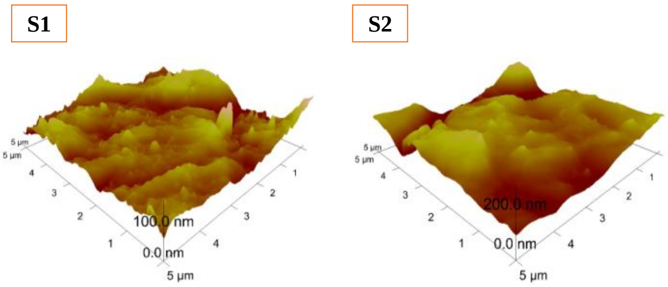

Fig. 1. *3D AFM images of the surface of the samples Sm 1, and Sm 2 with scan area 5 × 5 µm² and z-range, z = 100 nm and z = 200 nm*

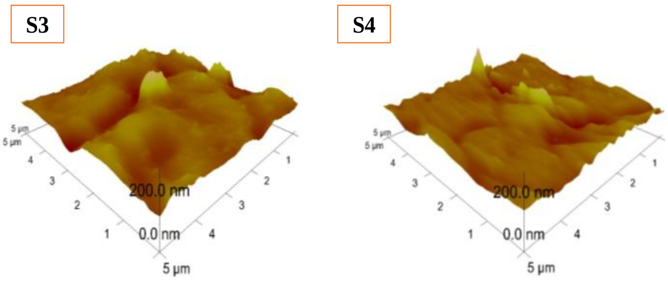

Fig. 2. 3D AFM images of the surface of the samples Sm 3, and Sm 4 with scan area 5 × 5 µm² and z-range, z = 200 nm

From the AFM images and the analysis of the roughness of the different samples it was found:

1. In the topography of the samples Sm 1 and Sm 2 with applied organic precursor of titanium isopropoxide, areas with a smooth surface as well as areas with a rougher surface are observed. The roughness value R_q for the scan surface at 5 µm for the coating S 1 is in the range between 20.5 nm and 41.1 nm, while the value for the coating S 2 is in the range between 43.7 nm and 31.6 nm.
2. In the topography of the samples Sm 3 and Sm 4 with applied organic precursor of titanium tetrabutoxide, again areas with a smooth surface as well as areas with a rougher surface are observed. The roughness value R_q for the scan surface at 5 µm for the coating S 3 is in the range between 23.2 nm and 47.7 nm, while the value for the coating S 4 is in the range between 20.9 nm and 51.6 nm.

4. Conclusions

The lowest corrosion rate have the samples marked Sm 2 and Sm 3. For the sample Sm 2, the corrosion rate during the first 50 hours is zero, and after the hundredth hour it is only 0.0007 - K [g].

It was observed, that the sample Sm 2 coating with a higher percentage of 1 at. % Sm_2O_3 has higher roughness values R_q at scann area 5 µm as compared to sample Sm 1 coating with a lower percentage of 0.5 at. % Sm_2O_3. While the sample Sm 4 coating with a higher percentage of 1 at. % Sm_2O_3, the roughness values R_q at scann area 5 µm are close to those for sample Sm 3 coating with a lower percentage of 0.5 at. % Sm_2O_3.

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