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AFM ANALYSIS OF MIXED TiO_2–ZrO_2 (1:1) SOL–GEL FILMS ON STAINLESS STEEL SUBSTRATE

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ABSTRACT
In this paper, sol-gel process, as a relative simple and low-cost method, was used for deposition of ceramic films on stainless steel substrate. Mixed TiO_2–ZrO_2 (1:1) sol–gel films were deposited on the X2CrNiMo17-12-2 (AISI 316L) austenitic stainless steel by dip coating method. For the sol preparation, titanium isopropoxide and zirconium butoxide were used as precursors, i-propanol as a solvent with addition of nitric acid as a catalyst, acetylacetone for peptization and water for hydrolysis. One-layer deposited films were annealed at the temperature of 401 °C and 600 °C.
The surface topography, as well as roughness parameters (R_a, R_q, R_{max} and the Z_{range} values) of sol-gel TiO_2–ZrO_2 films were analysed by atomic force microscopy (AFM).
Keywords: TiO_2–ZrO_2, sol-gel, stainless steel, AFM

1. INTRODUCTION
The progress in the area of manufacturing and extending the life expectancy of the constructional elements and tools, used in various domains of life, is taking place mostly thanks to the more and more common employment of the thin coatings deposition [1]. In order to improve properties of metallic materials, different ceramic coatings can be applied. Ceramic coatings can be deposited on metallic substrate by number of various techniques developed for this purpose. They include physical vapour deposition (PVD), chemical vapour deposition (CVD), electrochemical deposition, thermal spraying, plasma spraying and sol-gel processes, such as spin, dip and spray coating [2, 3]. Among them, sol-gel techniques are preferred for several reasons: they are simple, low temperature techniques (usually 200-600 °C), which avoid possible decomposition problems; can provide high purity, high quality and stoichiometric coatings; the adjustment of film thickness can be done easily; dip coating method is suitable for coatings of complex shaped substrate etc. [4, 5]. Surface morphology and roughness of prepared coatings is an important parameter. Fields of the AFM application are: physics of solids, thin-film technologies, nanotechnologies, micro- and nanotribology, microelectronics, optics, testing systems of the precision mechanics, magnetic record, vacuum engineering etc. [6]. During the last years, atomic force microscopy (AFM) has been used increasingly to investigate morphology of the coating surfaces [7, 8].
In the present paper, single layered sol-gel TiO_2–ZrO_2 films were deposited on AISI 316L austenitic stainless steel, using dip-coating technique. Surface morphology and roughness of prepared films were analyzed by means of atomic force microscopy (AFM).

2. EXPERIMENTAL PROCEDURE
2.1. Substrate
For this study, two steel plates (10×10×2 mm) were used as substrates. Bulk chemical composition of X2CrNiMo17-12-2 (AISI 316L) stainless steel was determined by glow discharge optical emission

spectroscopy (GDS 850A, Leco) and results in wt. % are presented in Table 1. Before the deposition of films, steel substrates were ground with SiC abrasive discs (180-1000 grit) and then polished with diamond paste (3 μm and 0.25 μm). Substrates were then ultrasonically cleaned in acetone and subsequently dried prior to the deposition process.

Table 1. The chemical composition of steel substrate, wt. %.

wt. %										
C	P	S	Si	Mn	Cu	Cr	Ni	Mo	V	Fe
0.026	0.0287	0.0021	0.37	1.42	0.345	16.38	10.53	2.17	0.1	balance

2.2. Sol-gel TiO_2–ZrO_2 films

For the preparation of sol (colloidal solution), the following components were used:
- 0.5 mol of titanium isopropoxide and 0.5 mol zirconium butoxide (ratio 1:1) as precursor,
- 0.8 mol acetylacetone as a chelating agent,
- 40 mol of *i*-propanol as a solvent,
- 0.05 mol of nitric acid as a catalyst,
- 5 mol of distilled water for hydrolysis.

The final precursor sol was yellow, transparent and homogeneous.
Stainless steel plates were coated by dip-coating technique using an in-house developed, electrically driven pulley system. The plates were once vertically immersed into the precursor sol with constant rate of 10 mm/min, left for 5 minutes in order to allow surface wetting, and withdrawn with the same rate. After immersion, the film was dried at room temperature for an hour and subsequently heated at 100 °C for an hour. Finally, coated steel substrates were annealed for 4 hours at 401 °C and 600 °C.

2.3. Characterization of sol-gel TiO_2–ZrO_2 films

The surface topography and roughness of the TiO_2-ZrO_2 films were determined by the Multimode AFM with a Nanoscope IIIa controller (Veeco Instruments Santa Barbara, CA) with a vertical engagement 125 μm scanner (JV). Contact mode imaging was performed under ambient conditions in air, by silicon tips (NP, Nom. Freq. 18 kHz, Nom. Spring constant of 0.06 N/m), and at a scan resolution of 512 samples per line. The linear scanning rate was optimized between 1.0 and 2.0 Hz at a scan angle of 0°. Images were processed and analyzed by means of the offline AFM NanoScope software, version 5.12r5. Roughness analysis software option was used to perform roughness analyses on 10 μm × 10 μm and 50 μm × 50 μm imaged surface area for each sol-gel TiO_2–ZrO_2 film. Results are presented as the R_a, R_q, R_{max} and the Z_{range} values.

3. RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the three-dimensional AFM micrographs and section profile of the surface of one layer TiO_2–ZrO_2 films calcined at 401 °C and 600 °C, respectively.
As shown in Figs. 1A, 1B, 2A and 2B the films, within the 10 μm × 10 μm and 50 μm × 50 μm imaging areas, are homogeneous, uniform, compact, free from cracks, smooth and have nano scratches (probably originating from the sample preparation stage). The scratches increased the roughness, but in generally the surface showed low topography variation. Also, for both deposited TiO_2–ZrO_2 films following roughness parameters were determined: R_a, R_q, R_{max} and Z_{range} values.

The roughness parameters of all investigated TiO_2–ZrO_2 films are presented in Table 2.
Obtained results indicate that all determined roughness parameters decrease with the increasing calcination temperature (for both scan size surface area).

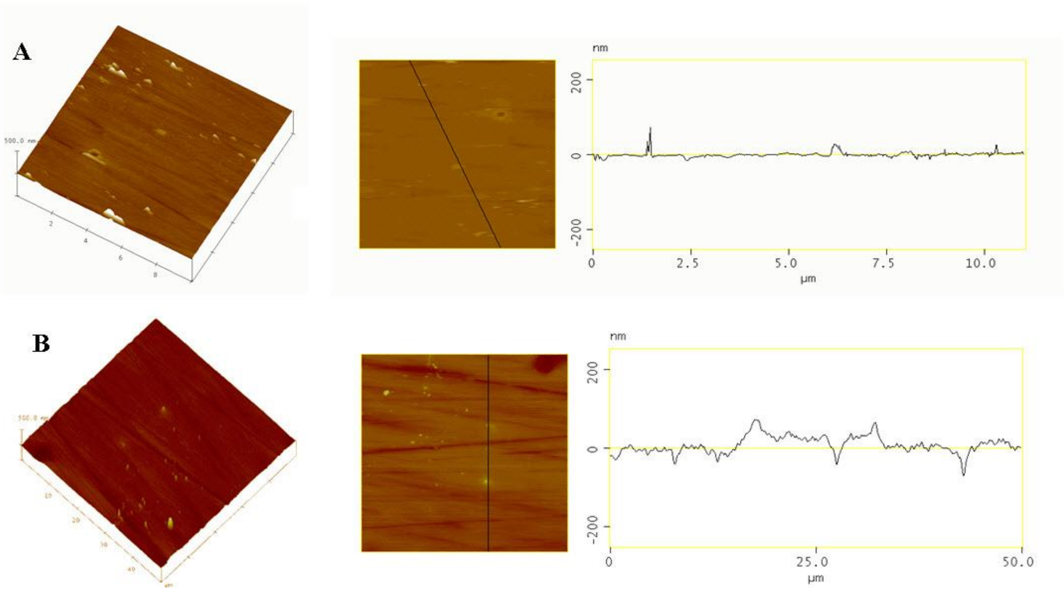

Figure 1. AFM analysis of deposited TiO_2–ZrO_2 films calcined at 401 °C; 3D image and AFM profile (A) 10 µm × 10 µm scan size and (B) 50 µm × 50 µm scan size

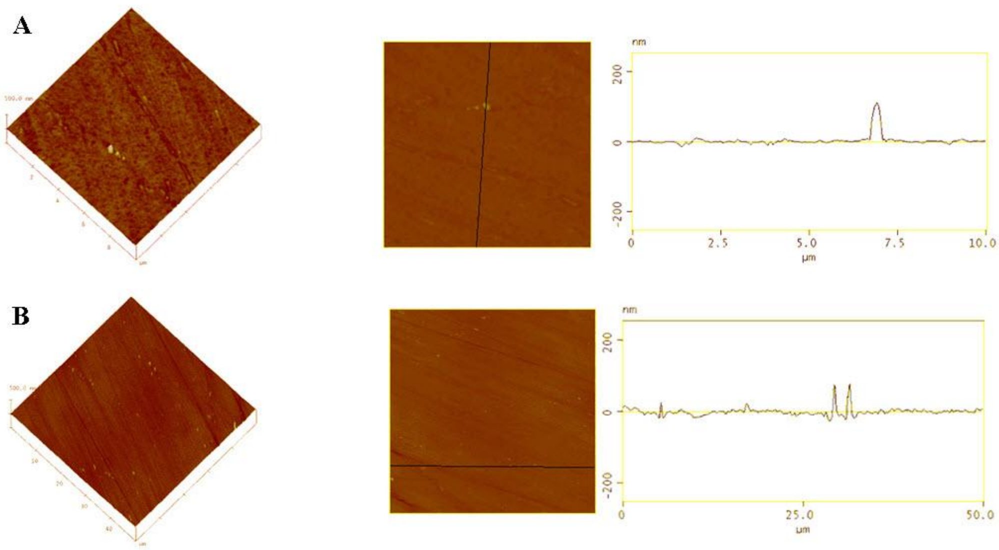

Figure 2. AFM analysis of deposited TiO_2–ZrO_2 films calcined at 600 °C; 3D image and AFM profile (A) 10 µm × 10 µm scan size and (B) 50 µm × 50 µm scan size

Tablica 2. Values of the roughness parameters of sol-gel TiO_2–ZrO_2 films annealed at 401 °C and 600 °C and different scan size

Annealing temperature		401 °C		600 °C	
Scan size		10 µm ×10 µm	50 µm ×50 µm	10 µm ×10 µm	50 µm ×50 µm
roughness parameters	Z_{max}, nm	462.1	461.0	140.7	300.0
	R_a, nm	13.5	11.6	3.6	5.8
	R_q, nm	19.1	17.5	5.3	8.0
	R_{max}, nm	504.0	461.6	140.7	300.8

4. CONCLUSIONS

Nanostructured sol-gel TiO_2–ZrO_2 films were deposited on stainless steel X2CrNiMo17-12-2 (AISI 316L) substrate by dip coating method. For preparation of sol, titanium isopropoxide and zirconium butoxide were used as precursors, *i*- propanol as a solvent, with the addition of nitric acid as a catalyst and acetylacetone for peptization.

Morphology as well as roughness parameters of deposited sol-gel TiO_2–ZrO_2 films after calcination at 401 °C and 600 °C were analysed by means of AFM. From the obtained results, the following conclusions can be drawn:

- AFM analysis of qualitative and quantitative data of the surface morphology of sol-gel TiO_2–ZrO_2 films indicated that the films surfaces are homogeneous, dense and free from cracks.
- By comparison of roughness parameters for sol-gel TiO_2–ZrO_2 films calcined at different temperatures, it can be concluded that sol-gel TiO_2–ZrO_2 film calcined at 401 °C has a higher roughness parameters than sol-gel TiO_2–ZrO_2 film calcined at 600 °C.

5. REFERENCES

[1] Dobrzanski L.A., Lukaszkowicz K.: Tribological behaviour of coatings deposited by reactive magnetron sputtering method, 11th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2007, Hammamet, Tunisia, 2007

[2] Dai, W.X., Chen, X., Li, E., Wang, X.X., Liu, P., Fu, X.Z.: Influence of pH value of TiO_2 sol on surface gloss of corresponding TiO_2 film coated on ceramic tiles, *Surf. Eng.* 25, 2009, 106-109.

[3] Fu, T., Wen, C.S., Lu, J., Zhou, Y.M., Ma, S.G., Dong, B.H., Liu, B.G.: Sol-gel derived TiO_2 coating on plasma nitrided 316L stainless steel, *Vacuum,* 86, 2012, 1402-1407.

[4] Gheriani, R., Chtourou, R.: Preparation of Nanocrystalline Titanium Dioxide (TiO_2) Thin Films by the Sol-Gel Dip Coating Method, *Journal of Nano Research* **2012**, *16*, 105-111.

[5] Wang, H., Wangb, Z., Honga, H.,. Yina, Y.: Preparation of cerium-doped TiO_2 film on 304 stainless steel and its bactericidal effect in the presence of sulfate-reducing bacteria (SRB), *Mater. Chem. Phys.* 124, 2010, 791-794.

[6] Bakasova D., Rusnakova S., Slabeycius J.: AFM analysis of special rubber blends, 13th International Research/Expert Conference "Trends in the Development of Machinery and Associated Technology" TMT 2009, Hammamet, Tunisia, 2009

[7] Zhang, Y., Gao, F.M., Gao, L.H., Hou, L., Jia, Y.F.: Study of tri-layer antireflection coatings prepared by sol–gel method, *J. Sol-Gel Sci. Technol.* 62, 2012, 134-139.

[8] Šegota, S., Ćurković, L., Ljubas, D., Svetličić, V., Fiamengo Houra, I., Tomašić, N.: Synthesis, characterization and photocatalytic properties of sol-gel TiO_2 films, *Ceramics International,* 37(4) 2011, 1153-1160.