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The Effect of TiO_2 Layers on the Surface Properties of Materials

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TiO_2-based thin layers are used to improve or change the surface properties of various materials. The work deals with the effect of TiO_2 layers on the surface properties of selected substrates. The layers were prepared by the sol-gel method using the dip-coating technique on glass and stainless steel. The sol was prepared in "titanium isopropoxide - isopropyl alcohol - acetyl acetone - water - catalyst" system, whereas as catalyst was used nitric acid or acetic acid. The morphology and topography of the surfaces of the uncoated and coated substrates were evaluated by atomic force microscopy. Scanning electron microscopy was used to determine the layer thickness. The effect of TiO_2 layers on the surface properties of materials was also evaluated using wetting angles, surface energy and its polar and dispersion components. Based on the results, especially the higher surface energy value, we can conclude that the TiO_2 layer influenced the surface properties of the studied solid materials.

Keywords: sol-gel method, TiO_2 layers, surface properties, roughness

1 Introduction

In recent years, thin TiO_2 layers have been intensively studied due to their wide potential use not only in photocatalysis [1], but the application of thin TiO_2 layers on the surface of glasses in the automotive industry due to their self-cleaning properties [2], or on the surface of metals as a surface protection against corrosion, appears to be very promising [3]. A thin layer of TiO_2 on the surface of the material can fulfil a dual function. The first one is the photocatalytic function, in which there is a high recombining ratio of photoinduced electron holes in the film that move to the surface [4] and interact with daylight to breakdown the organic dirt. The second one is the hydrophilic function, which means that rainwater droplets hit the glass and spread evenly, running off in a "sheet" and taking the loosened dirt with it, and also drying quickly without leaving streaks [5].

Solid materials can come into contact with various liquids (most often water), therefore research in the field of surface properties is very important, especially wetting of the surface of materials. Research in the field of self-cleaning surfaces and/or materials is particularly interesting, mainly because of their potential applications in practise. Self-cleaning of a material surface is the situation when water drops of a given volume can undergo sliding, rolling, or both if the substrate is tilted beyond a critical angle. Water droplets slide across the surface due to a significant reduction in surface tension between the water droplets and the self-cleaning surface. Therefore, dust particles are easily washed off the surface of the material [6].

One of the most common causes of damage to the surface of metal materials is damage caused by corrosion. Metal corrosion cannot be completely eliminated, but its intensity can be reduced by choosing suitable materials for a specific use (e.g., in the automotive industry), using new alloys, applying corrosion inhibitors, or using protective thin layers and coatings on the surface of metals, especially in an aggressive environment. Stainless steels are known for their good resistance to corrosion in many corrosive environments but are prone to localised corrosion in the presence of chloride ions [7–9].

Different oxide layers, such as TiO_2, Al_2O_3, ZrO_2, SiO_2, can be formed on the surface of glasses and metals to improve their surface properties [10]. There are several techniques for forming thin oxide films on glass and metal substrates, such as chemical vapour deposition (CVD) [11], physical vapour deposition (PVD) [12], plasma deposition [13], electrochemical deposition [14] and the sol-gel process [15]. Traditionally, surface pretreatments to increase the corrosion resistance of metals by applying thin layers, and coatings usually release toxic fumes. Therefore, the use of the sol-gel method as a surface protection appears to be a more ecological alternative. The sol-gel method, also known as chemical solution deposition, is a wet-chemical technique that involves the following steps: hydrolysis and polycondensation, gelation, ageing and drying. A sol-gel coating can be applied to a metal substrate through various techniques, such as dip-coating, spin-coating and spraying [16]. Other advantages of the sol-gel method include the low cost of experimental equipment, laboratory processing temperature, good homogeneity, and the use of starting compounds that do not introduce impurities into the final product, and thus the sol-gel method becomes a "green" waste-free technology. Due to these advantages, the sol-gel method is one of the most suitable technologies for the preparation of thin layers [17].

In the work, the influence of TiO_2 layers, prepared from sols with different acid catalysts, deposited on glass and steel substrates on their surface properties, such as morphology, topography, surface wettability and free surface energy, was monitored.

2 Experimental

2.1 Preparation of sols

TiO_2 sols were prepared using isopropyl alcohol (IPA, 99.7 %, Centralchem) as solvent, titanium isopropoxide (iPTi, 98 %, Acros Organics) as TiO_2 precursor, acetyl acetone (AcAc, 99.5 %, Penta) as stabiliser, nitric acid (NA, 65 %, Centralchem) or acetic acid (AA, 99 %, Centralchem) as catalyst, and distilled water (H_2O, FPT). Molar composition of two prepared sols is shown in Table 1.

Tab. 1 *Molar composition of TiO_2 sols*

Sol	Component					
	iPTi	AcAc	NA	AA	H_2O	IPA
TiO_2 (NA)	0.050	0.100	0.050	-	0.200	0.600
TiO_2 (AA)	0.050	0.050	-	0.005	0.200	0.695

The sols were prepared at room temperature according to the scheme shown in Fig. 1. The first solution, designed as SA, was prepared by mixing of isopropyl alcohol (50 % of IPA), acetyl acetone and titanium isopropoxide. After 15 minutes of mixing, the second solution, designed as SB, containing isopropyl alcohol (50 % of IPA), water and acid catalyst was added. The final TiO_2 sol, designed as SAB, was mixed for 2 hours.

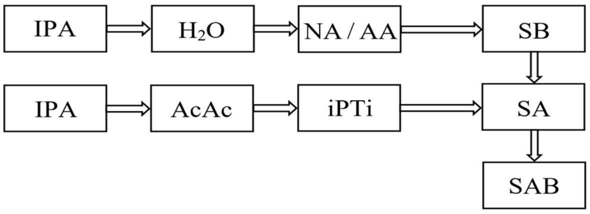

Fig. 1 *Scheme for the preparation of TiO_2 sols*

2.2 Preparation of layers

Two substrates with dimensions of 25×75×1 mm were used in experiments – a commercial microscope slide glass (ISO 8037/1) and chromium nickel austenitic stainless steel (AISI 304) [18]. The substrates were carefully cleaned with detergent, distilled water and isopropyl alcohol. Finally, they were dried at 80 °C for 20 minutes.

One day after preparation of the sols, the substrates were coated with the sols by the dip-coating technique. The holding time in the sol and the withdrawal rate were 15 s and 40 $mm.min^{-1}$, respectively. The coated substrates were dried for 1 hour at 80 °C, heated for 1 hour at 450 °C with heating rate of 10 $°C.min^{-1}$ and then left to cool to room temperature.

2.3 Methods of characterisation

Surfaces of prepared layers were observed by atomic force microscopy (AFM), using a NT-206 equipment (Microtest machines Belarus) [19]. For measurements in contact mode at room temperature and humidity, Si_3N_4 tip (Micro Masch NSC 11/AlBS) with spring constant of 3 $N.m^{-1}$ was used. Each layer was measured five times at randomly chosen places. Morphology and topography were processed by the Surface Explorer 1.0.8.65 software.

Semiquantitative chemical analysis of substrates and layers was performed using an energy dispersive X-ray fluorescence spectrometer EDX-7000 (Shimadzu).

The thickness of the layers was determined by a TESCAN VEGA 3 scanning electron microscope.

The sessile drop technique was used to determine the contact angle of distilled water and diiodomethane At least 10 drops of the test liquid with a volume of 5 µl were dropped onto each surface of the substrate and the film at different points of the surface. All contact angle values were tested using the Grubbs test for outliers, which were excluded during the further evaluation of surface free energy. Using the Fowkes method [20], the free surface energy and its polar and dispersion components were calculated from the contact angle values.

3 Results and discussion

3.1 Surface topography and morphology

Using AFM Surface Explorer software, 2D and 3D images as well as roughness values for the surface of the substrates and TiO_2 layers coated on these substrates were obtained. Figs. 2 and 3 show 2D and 3D images of surface of uncoated substrates and TiO_2 layers deposited on the selected substrates – glass and steel, respectively.

The surface of uncoated glass consists of smaller granular formations relatively evenly distributed (Fig. 2a). There are also larger formations that are unevenly distributed in the layer. The application of the layers to the glass changed the morphology of the surface. In the case of the layer prepared from sol with nitric acid, smaller irregularities were smoothed out, but large grainy formations remained there (Fig. 2b). Compared to uncoated glass and the layer prepared from sol with nitric acid, the surface of the layer prepared from sol with acetic acid is different: there are evenly distributed small granular formations (Fig. 2c).

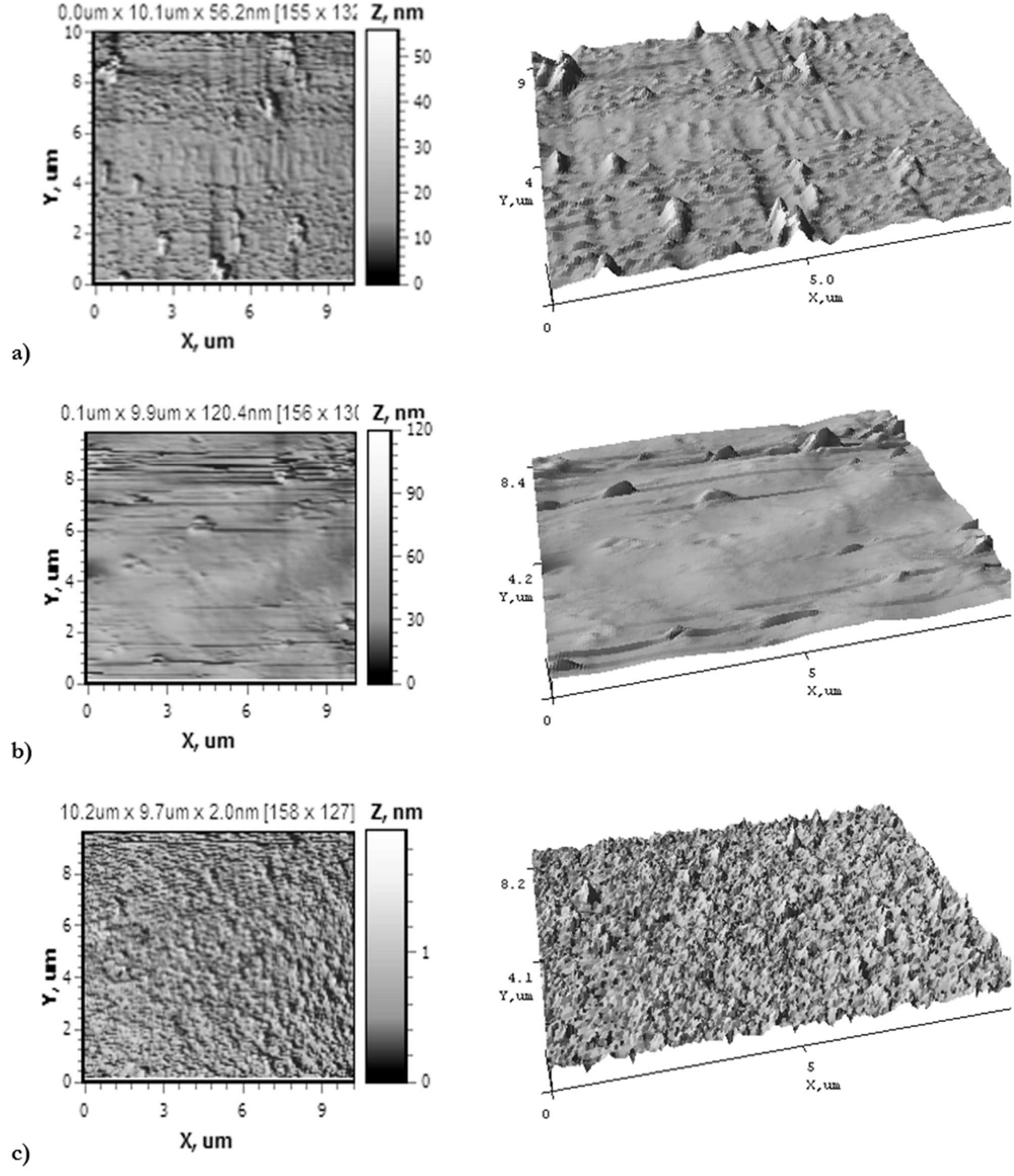

Fig. 2 *2D and 3D images of the surface of: a) uncoated glass and glass coated with TiO_2 layers prepared from sol with (b) nitric acid and (c) acetic acid*

The surface of stainless steel without a layer (Fig. 3a) is significantly wrinkled, with sharp elevations of an irregular shape. On the surface of the steel with a layer prepared from sol with nitric acid (Fig. 3b), there is a smaller number of protruding formations, but the applied layer still copies the periodic transverse irregularities. Although the layer prepared from the sol with acetic acid continues to copy the surface of the steel (Fig. 3c), sharp formations on its surface occur only rarely.

Table 2 shows the *rms*-roughness values. In the case of both TiO_2 layers, the deposition of the layer on the steel substrate caused smoothing of the surface and a decrease in the *rms*-roughness value. In the case of a layer prepared from sol with nitric acid and applied to a glass substrate, there was an increase in the *rms*-roughness value due to the significant irregularities observed on the surface of this layer (Fig. 2b). The layer prepared from a sol with acetic acid and applied to glass has a significantly lower *rms*-roughness value than the substrate itself, which is in accordance with the observed morphology of the surface of this layer (Fig. 2c).

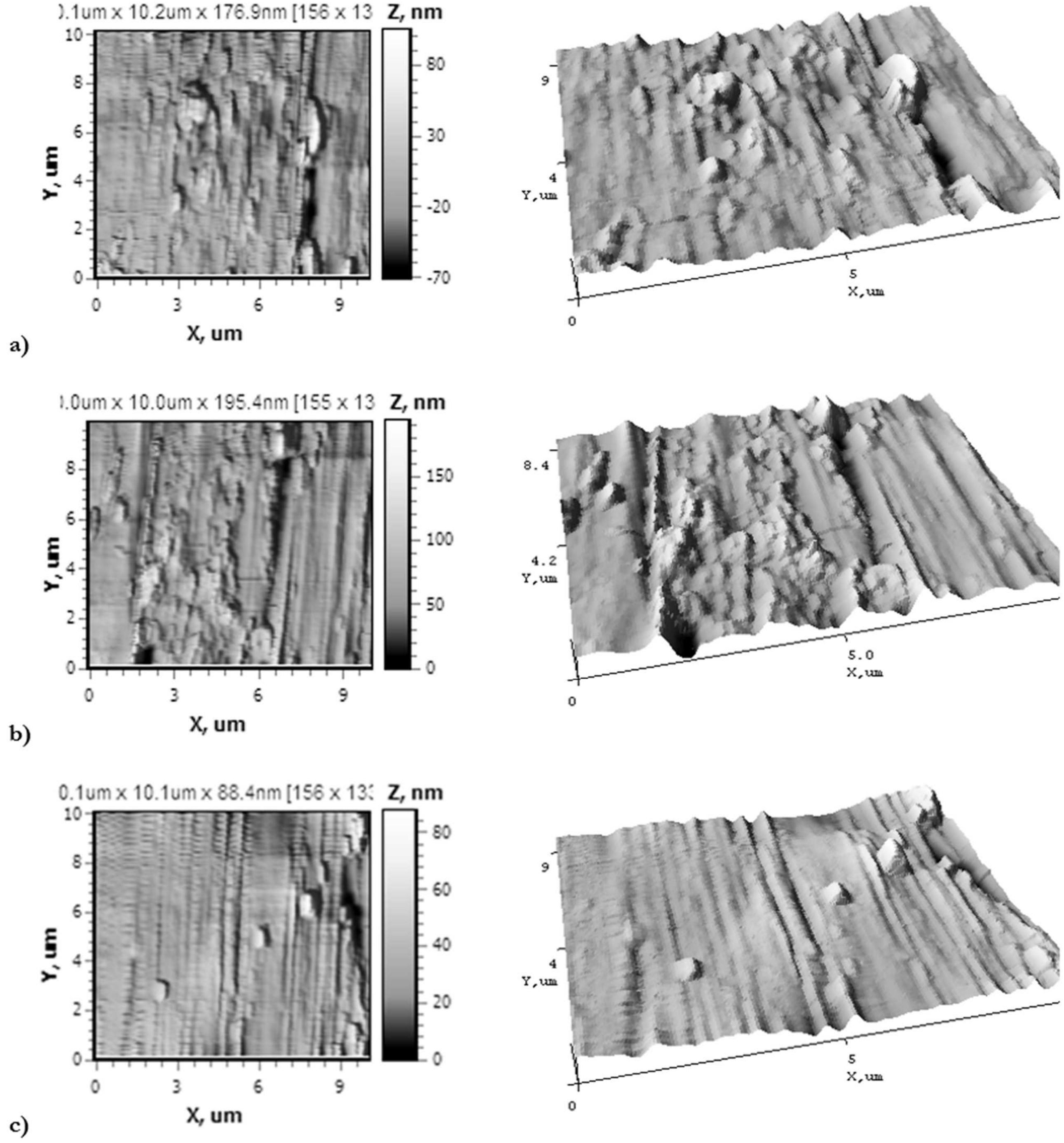

Fig. 3 *2D and 3D images of the surface of: a) uncoated stainless steel and stainless steel coated with a* TiO_2 *layer prepared from sol with (b) nitric acid and (c) acetic acid*

Tab. 2 *Mean rms-roughness values of surface of substrates and TiO_2 layers*

Surface	rms-roughness (nm)
uncoated steel	22.08 ± 5.40
steel/TiO_2(NA)	17.75 ± 4.57
steel/TiO_2(AA)	13.82 ± 5.05
uncoated glass	2.64 ± 1.03
glass/TiO_2(NA)	9.79 ± 3.01
glass/TiO_2(AA)	3.21 ± 0.03

3.2 EDX analysis

The composition of the steel used and both TiO_2 layers coated on the given substrate, determined by EDX analysis, is shown in Table 3. The results of the EDX analysis confirmed the presence of titanium in the layers prepared from both TiO_2 sols, the steel substrate did not contain any titanium.

Tab. 3 *Elemental composition of an uncoated and TiO_2 coated steel substrate*

		Fe	Cr	Ni	Mn	Ti	Cu	Ca	Mo	V
steel	**wt.%**	70.92	18.43	8.44	1.77	-	0.27	0.04	0.10	0.04
	s.d.	0.21	0.09	0.09	0.02	-	0.01	0.02	0.01	0.01
steel/TiO_2(NA)	**wt.%**	70.61	18.11	8.48	1.86	0.51	0.27	0.05	0.10	0.03
	s.d.	0.21	0.09	0.10	0.02	0.02	0.01	0.02	0.01	0.01
steel/TiO_2(AA)	**wt.%**	70.81	18.01	8.48	1.84	0.39	0.26	0.07	0.10	0.05
	s.d.	0.21	0.09	0.10	0.02	0.01	0.01	0.02	0.01	0.01

s.d. – standard deviation

3.3 SEM microscopy

The thickness was measured by SEM as shown in Fig. 4. The thickness values of the layers deposited on the steel surface was mainly in the range of 0.20 to 0.25 µm. The thickness of layers is not uniform mainly due to the uneven surface of the steel substrate.

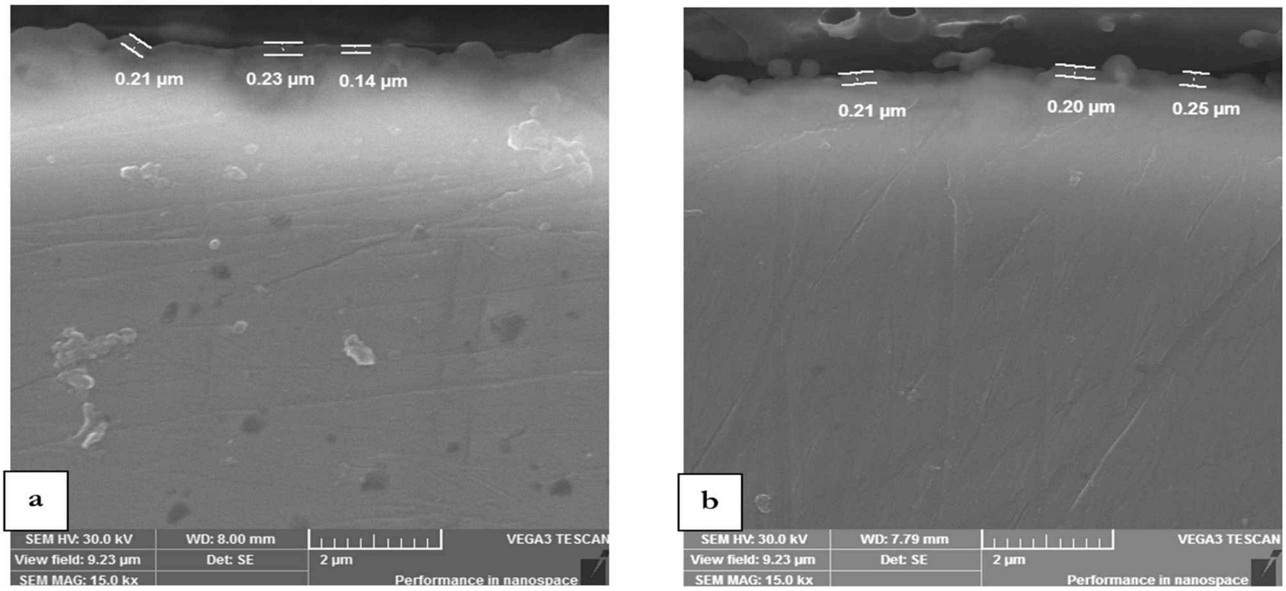

Fig. 4 *SEM images of the cross section of TiO_2 layer deposited on the steel substrate (zoomed 15000×); TiO_2 sol prepared with (a) nitric acid and (b) acetic acid*

3.4 Contact angle and surface free energy

The surface free energy (SFE) was calculated from the contact angles of distilled water and diiodomethane. After measurement of drops on the surface, it was shown that the contact angle of distilled water on uncoated glass had a value of 23.08°, on glass with TiO_2(NA) layer its value was 4.69°. On a glass sample with a TiO_2(AA) layer, the contact angle of distilled water could not be measured because a drop of distilled water completely wetted the surface of the layer. When comparing uncoated glass and glass with a layer, we can conclude that the TiO_2(NA) layer caused the surface to become more hydrophilic.

For the uncoated stainless steel, the value of the contact angle of distilled water was 102.97°. The contact angle for stainless steel with a TiO_2(NA) layer had a value of 64.94°. For the stainless steel with a TiO_2(AA) layer, its value was 67.54°. It can be seen that the TiO_2(NA) layer and the TiO_2(AA) layer reduced the value of the contact angle compared to uncoated stainless steel. However, both layers showed very similar values of the contact angle of the distilled water.

From the calculated surface energy values, which are shown in Fig. 5, it can be seen that the uncoated and coated glass does not show large differences between the values of the polar and dispersion components of the surface free energy. The difference in the values of the polar component for uncoated glass and glass with a layer was 0.77 $mJ.m^{-2}$. For the dispersion component of the same sample, the difference is slightly higher, namely 5.15 $mJ.m^{-2}$. For uncoated stainless steel, it can be seen that the dispersive component mainly prevails in the free surface energy value, and the polar component is at the level of the standard deviation. For stainless steel with a TiO_2 layer, the free surface energy is at the level of 51.33 $mJ.m^{-2}$ for the TiO_2(NA) layer and 49.96 $mJ.m^{-2}$ for the TiO_2(AA) layer, and simultaneously, the values of the polar and dispersive components of the free surface energy are very similar. The results of the SFE measurement confirmed that the TiO_2 layer on the stainless steel substrate smoothed out surface irregularities and, therefore, it can be assumed that it will improve the corrosion resistance of the surface of the given stainless steel.

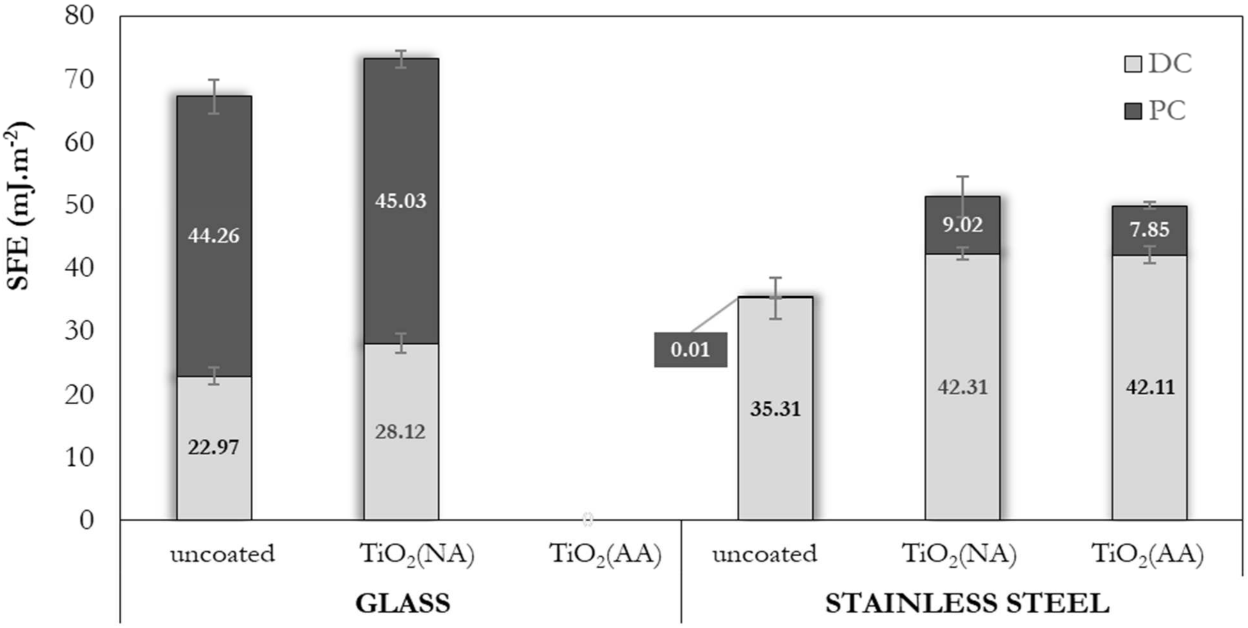

Fig. 5 *Surface free energy (SFE) of the uncoated and coated TiO_2 layer of glass and stainless steel prepared from sol with nitric acid (NA) and acetic acid (AA), PC – polar component of SFE, DC – dispersive component of SFE*

4 Conclusion

The work deals with the investigation of the influence of TiO_2 layers prepared by the sol-gel method applied on a glass substrate and stainless steel on their surface properties. EDX analysis confirmed that the layers applied to the substrates contain titanium when both sols are used for their preparation. The thickness of the layers applied to the surface of the stainless steel was in the range of 0.20 to 0.25 µm.

By applying a layer to the surface of the glass, the morphology of the surface changed. In the case of the layer prepared from the sol with nitric acid, there was a slight smoothing of the unevenness. On the surface of the layer prepared from the sol with acetic acid, very small granular formations are evenly distributed and the surface is smooth, which is also confirmed by the roughness values (approximately 10 nm in the case of the layer prepared from the sol with nitric acid and 0.2 nm in the case of the sol prepared with acetic acid).

Applying a layer on the surface of stainless steel resulted in a slight smoothing of the surface, and the layer copies the surface irregularities. By applying the layer, the roughness of the surface was reduced compared to the original uncoated surface from a value of 22 nm to approx. 18 and 14 nm in the case of layers prepared from sol with nitric acid and acetic acid, respectively.

The contact angle values of distilled water and SFE for the glass substrate confirmed the results obtained by AFM. The TiO_2 layer caused the surface changed to hydrophilic and water droplets would easily run down it. Therefore, the TiO_2 layers studied could be used as a surface treatment for car windshields. The TiO_2 layers in the stainless steel increased the values of the SFE dispersion component. It can be assumed that used TiO_2 layer on studied metal material could improve its corrosion resistance.

Acknowledgement

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