The influence of corrosion of TiO$_2$ films on their surface properties

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Abstract. The work deals with the influence of TiO$_2$ films corrosion in distilled water on the surface properties of TiO$_2$ films. Films were prepared from the sol in "Ti(i-PrO)$_4$ - IPA - H$_2$O - HNO$_3$" system by dip-coating technique. The surface properties of films were observed using atomic force microscopy and sessile drop method. The morphology and rms-roughness of prepared films were evaluated. On the basis of Fowkes method, the contact angles of films, using distilled water and diiodomethane, were used for determination of surface free energy and its polar and dispersion components. The given surface properties of TiO$_2$ films were compared from the aspect of their preparation temperature (200, 300 and 400 °C) as well as corrosion in water. It was observed, that the film preparation temperature did not have noticeable influence on studied surface properties for non-corroded films. The influence of corrosion was observed only for films prepared at temperature of 300 °C and 400 °C. The corrosion in water influenced the morphology of film surface, increased the roughness, contact angle for water as well as the value of dispersion component of surface free energy.

1. Introduction

The materials based on TiO$_2$ have a big potential in preparation of films with various functions. TiO$_2$ films have an utilisation in many different applications, from solar systems [1, 2] through self-cleaning [3, 4] or protection films [5, 6] to their utilisation for modification of textile [7, 8]. The utilisation of TiO$_2$ materials is in a great measure influenced by properties of TiO$_2$ [1, 2, 6, 9–11] – photocatalyticity, hardness, corrosion resistance, biocompatibility or hydrophilicity which is influenced by the state of surface, morphology and roughness. It is necessary to know the behaviour of TiO$_2$ films in various corrosion (real or model) media and how the corrosion influences of film surface state [4–6] in order to obtain the protection function of TiO$_2$ films.

For preparation of protection films based on oxides, the sol-gel method is commonly used. At low temperatures, this method allows the preparation of high-pure homogeneous films with required properties [12–14]. For the reasons mentioned above, this work deals with the study of the influence of corrosion on the selected surface properties of TiO$_2$ films prepared by the sol-gel method.
2. Experiment

2.1. Sol preparation
For preparation of TiO\(_2\) sol, titanium isopropoxide (98%, Ti(iPr)\(_4\)), isopropyl alcohol (p.a., IPA), nitric acid (66%, HNO\(_3\)) and distilled water (H\(_2\)O) were used. The molar composition of the solution used for preparation of sol was \(x(\text{TiO}_2) : x(\text{HNO}_3) : x(\text{H}_2\text{O}) : x(\text{IPA}) = 0.05 : 0.09 : 0.21 : 0.65\), respectively. The sol was prepared from three solutions, which were stirred for 15 min, according the procedure given in [15, 16]. The final sol was stirred for 30 min.

2.2. Film preparation
The films were prepared by dip-coating technique on glass substrates (microscope slide glasses). Before coating, the substrates were cleaned by the following procedure – cleaning with detergent, rinsing with water, distilled water and isopropyl alcohol, and then drying at 105 °C for 15 min.

The films were prepared after one, two and three days from sol preparation at withdrawn speed of 30 mm min\(^{-1}\). The films were dried at 105 °C for 15 minutes and then heated at speed of 10 °C min\(^{-1}\) and after that, the individual films were heat treated at 200 °C, 300 °C or 400 °C for 1 hour.

2.3. Film corrosion
The individual films were inserted into polypropylene flasks filled with 100 ml of distilled water. The corrosion of films was in progress in dryer at 80 °C for 5 hours. After corrosion, the films were rinsed with water, distilled water and isopropyl alcohol, and dried at 80 °C for 15 min.

2.4. Surface properties measurements
The observation of film surface was performed by NT-206 atomic force microscope (Micro test Machines Belarus) which operated in contact mode in the air at room temperature. The MikroMasch HQ:NSC18/AIBS cantilever with spring constant of 2.8 N m\(^{-1}\) was used. Each film was measured in several selected places and AFM 15 μm \(\times\) 15 μm images were obtained. The surface morphology and topography (rms-roughness) were evaluated by SurfaxeXplorer 1.0.8.65 program according to the procedure described in [15]. However, in this case, there was a little difference in the image adjustment – the values for heights of unevenness were assigned to the plane, that is defined by three lowest height values for a given image, and to the line defined by the two lowest height values for a given scan in the direction of scanning and in the direction perpendicular to scanning.

For determination of the contact angle on the surface of films, the sessile drop method was used. As measurement liquids, the distilled water and diiodomethane were used. Ten drops of measurement liquid with the volume of 10 μl were uniformly dropped on the each film. The profile of drop was recorded by digital CCD camera and contact angle was calculated by help of Matlab software.

3. Results and discussion

3.1. Surface morphology and roughness
The surface morphology of the prepared films was evaluated visually on the basis of 2D AFM images. Figure 1 shows the 2D surface morphologies of non-corroded TiO\(_2\) films which were prepared at different preparation temperatures. The surface of all non-corroded films has a relatively fine structure only with small bumps. However, several little cavities are observed on the surface of films prepared at temperature of 200 °C (figure 1a).

Figure 2 shows the 2D surface morphologies of TiO\(_2\) films prepared at different preparation temperatures after corrosion in distilled water. After corrosion, the surface morphology of films prepared at temperature of 200 °C (figure 2a) is comparable to the morphology of films before corrosion (figure 1). After corrosion, the surface morphology of films prepared at temperatures of 300 and 400 °C (figures 2b and 2c) is quite different in comparison with non-corroded films as well as corroded films prepared at 200 °C. On the surface of given films, there is a lot of cavities which are...
non-uniformly located. Besides the cavities, there is a lot of grooves on the surface of film prepared at temperature of 400 °C after corrosion (figure 2c). These grooves are non-uniformly located on the surface and they have various length and depth.

Figure 1. 2D AFM images of film surfaces before corrosion; TiO$_2$ films prepared at 200 °C (a), 300 °C (b), 400 °C (c).

Figure 2. 2D AFM images of film surfaces after corrosion; TiO$_2$ films prepared at 200 °C (a), 300 °C (b), 400 °C (c).

The dependence of the surface roughness, also called the rms (root mean squared) roughness [15], on the preparation temperature of films as well as films corrosion in water is shown in figure 3. As the preparation temperature increases, the rms-roughness of non-corroded films decreases from value of (1.50 ± 0.05) nm to (0.96 ± 0.03) nm. This reduction in rms-roughness can be explained by densification of films during thermal treatment. The corrosion did not have the influence on the rms-roughness of films prepared at temperature of 200 °C. However, after corrosion, the rms-roughness of
films prepared at temperatures of 300 °C and 400 °C was increased from value of (1.4 ± 0.2) nm to value of (2.8 ± 0.2) nm and (2.7 ± 0.1) nm, respectively.

![Figure 3](image)

**Figure 3.** The influence of preparation temperature and corrosion on the rms-roughness of prepared TiO$_2$ films.

3.2. Contact angle and surface free energy

The recorded profiles of drops of water and diiodomethane on prepared TiO$_2$ films (figure 4) were used for calculation of contact angles and figure 5 shows the dependence of the contact angle of measurement liquids on the preparation temperature of films as well as films corrosion in water.

The contact angle of water on the film surface decreased from value of ~81° to ~71° when the preparation temperature of films increased from 200 to 300 °C. The further increasing of temperature did not have the significant influence on contact angle for water. In relation to contact angle for diiodomethane, the little influence of preparation temperature of films was observed only in the case of increasing temperature from 300 to 400 °C, when the value of contact angle increased from ~43° to ~46°.

The corrosion with water caused the increasing of contact angle for water (in average of 9°) and the decreasing of contact angle for diiodomethane (in average of 13°). The films prepared at 200 °C were the exception – for these films, the contact angle for water after corrosion was almost the same as before corrosion.

![Figure 4](image)

**Figure 4.** The drop of distilled water (a) and diiodomethane (b) on TiO$_2$ film prepared at 300 °C.
Figure 5. The influence of preparation temperature and corrosion on the contact angle for distilled water and diiodomethane for prepared TiO$_2$ films.

For calculation of polar and dispersion components of surface free energy (SFE) of prepared TiO$_2$ films, the Fowkes theory [17] was used. The polar and dispersion components of SFE were calculated according to [16] using measurement of contact angle for liquid with dominant polar component (water) and liquid with dominant dispersion component (diiodomethane) [18]. The dependence of the surface free energy and its components on the preparation temperature of films as well as films corrosion in water is shown in figure 6.

Figure 6. The influence of preparation temperature and corrosion on the surface free energy and its dispersion and polar component for prepared TiO$_2$ films.

For non-corroded films, the higher value of SFE was observed only for films prepared at temperature of 300 °C. After corrosion, the values of SFE increased only for films prepared at temperatures of 200 and 400 °C, while the values of their SFE increased to the level of SFE value for films prepared at 300 °C (before as well as after corrosion).

All prepared films had high value of dispersion component of SFE (near to 38 mJ m$^{-1}$) and low value of polar component of SFE (in the range about 4–8 mJ m$^{-1}$). The preparation temperature of films did not have significant influence on value of dispersion component of SFE for non-corroded as
well as corroded films. The difference between values of dispersion component of SFE before and after corrosion in water is noticeable. After corrosion, the values of dispersion component of SFE increased in all films in an average of 6 mJ m⁻¹.

For films prepared at 200 °C, the value of polar component of SFE was not change after corrosion. The preparation temperature of film had the influence on the value of polar component of SFE only during temperature change from temperature of 200 to 300 °C, and mentioned change was observed for non-corroded as well as corroded films. After given change of preparation temperature, the value of polar component of SFE increased from ~3.6 mJ m⁻¹ to ~7.7 mJ m⁻¹ for non-corroded films but it decreased from ~3.8 mJ m⁻¹ to ~1.9 mJ m⁻¹ for corroded films.

The changes in studied surface properties, especially when the preparation temperature of films was changed from 200 to 300 °C, are related to the processes taking place in TiO₂ films during their thermal treatment. On the basis of thermal analysis of xerogels for studied system (it is not shown in this work), it was found that the processes associated with weight loss are completed up to 400 °C. However, only about 43% and 80% of all mentioned processes are completed up to 200 °C and 300 °C, respectively. Mentioned fact can be used for explanation of the behavior of the films prepared at temperature of 200 °C during corrosion in water as well as the effect of corrosion on the studied surface properties. After corrosion of films prepared at 200 °C, there is not change in surface morphology and roughness as well as in the value of polar component of SFE and it indicates that at this temperature, the significant amount of organic non-polar substances is in films. During corrosion, these organic non-polar substances have "hydrophobic" behaviour – there is not any change in the surface properties of films. However, in the films prepared at 300 and 400 °C, the processes associated with the removal of solvent and other organic non-polar substances are almost completed, and therefore, these films have the higher value of polar component of SFE. The decrease in the polar component of SFE after corrosion by water is caused by the "hydrophilicity" of the surface of these films when they interact with corrosion medium with polar character – water. Thus, the surface of film becomes poor in relation to "parts" that leave the films as corrosion products and the surface morphology is changed (cavities in AFM images).

4. Conclusion
The surface properties of TiO₂ films prepared from the sol in "Ti(i-Pro)₄ - IPA - H₂O - HNO₃" system were studied from the aspect of preparation temperature of films as well as corrosion in water. All prepared TiO₂ films had a smooth surface.

The preparation temperature of films influenced the studied surface properties only during the temperature change from 200 °C to 300 °C. When the preparation temperature increased, the roughness of film surface as well as contact angle for water decreased, and moreover, the surface free energy, or more precisely said, its polar component increased.

The studied surface properties of films prepared at 200 °C were not influenced by the corrosion in water but the corrosion influenced the surface properties of films prepared at 300 and 400 °C in similar way. After corrosion, the surface morphology of the given films was changed and surface roughness as well as the contact angle of water increased. Moreover, the corrosion influenced the surface free energy of these films from aspect of surface polarity – the dispersion component of surface free energy increased.

5. References
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