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Modification of the titanium implants surface with TiO2 coatings obtained by sol-gel method via dip-coating

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Abstract. Within the framework of the study, TiO2 coatings were obtained by sol-gel method via dip-coating. For the films obtaining, manual drawing the substrate from the solution at a relatively high rate of 30 mm / min and automated drawing from the solution at low drawing rates (from 1 to 10 mm / min) were used. The morphology of coatings has been studied by scanning electron microscopy. The influence of the mode and the rate of drawing of the substrate from the solution on the films morphology was demonstrated. Analysis of the data showed, that the surface morphology of the coatings obtained at lower drawing rates by an automated method is much more homogeneous - the titanium dioxide films completely repeats the topography of the substrate surface, there are practically no fissures. Qualitative coatings of titanium dioxide, completely replicating the surface relief of the substrate, can be obtained by this method. Selection of the substrate drawing rate allows reducing the influence of the substrate topography and avoiding the appearance of crystallization centers, and as a consequence, the appearance of defects in the morphology of coatings, such as fissures or microparticles.

1 Introduction

To date, great attention is being paid to the problems of obtaining and studying the properties of thin-film materials. In particular, thin films of titanium dioxide are one of the promising nanomaterials due to a combination of such properties as chemical inertness and stability, high biocompatibility, transparency in the visible range of the spectrum, photocatalytic activity. These and other properties allows finding a variety of applications for TiO_2 based coatings in various fields: in optics to create optical filters and functional coatings [1], in medicine as biocompatible coatings [2], as well as coatings with antibacterial effect [3], in electronics for the creation of photoconverters and functional coatings for solar cells [4], coatings, that have photocatalytic activity for the harmful organic contaminants decomposition [5,6], in the gas sensors [7].

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The structured surface of the implant is the key to optimal osseointegration. The change in the micro- and nano-texture of the implant surface and its roughness, obtained by the nano-processing of the contact element, makes it possible to increase its contact area. The increase in the implant surface area provides a more intensive absorption of plasma proteins on the contact surface after its installation substantially increases the hydrophilicity of the surface of the inserted element upon contact with the biotissues of the prosthetic bed and significantly improves the osseointegration of the dental implants. The possibility of implanting nanostructured surfaces into clinical practice allows implantation even at unfavorable clinical conditions [8].

Coatings of titanium dioxide can be obtained by various methods, such as spray-coating [9], sputter deposition [10], spin-coating [11] sol-gel method [1, 2, 4, 6, 7]. Sol-gel method has many advantages over the listed methods, such as economy, technological simplicity, the possibility of obtaining coatings on products of almost any shape, the possibility of varying the composition of coatings in a wide range, the production of composite coatings based on titanium dioxide. In this case, a high quality of the films can be achieved, comparable with the gas-phase deposition methods.

In this regard, the urgent task is to develop new economical methods for obtaining thin TiO_2 films on the surface of implants and to study the effect of synthesis conditions and subsequent processing of films on their properties.

2 Experimental

2.1 Obtaining of TiO2 films via dip-coating

In this work, TiO_2 coatings were obtained by dip-coating, which is one of the varieties of the sol-gel method. The advantages of this method are the simplicity and the ability to control the film thickness by varying the rate of drawing the substrate out of the solution, the number of drawing cycles and the concentration of the film-forming agent in the solution. The scheme of the experimental setup used to obtain thin TiO_2 films is shown in Fig. 1.

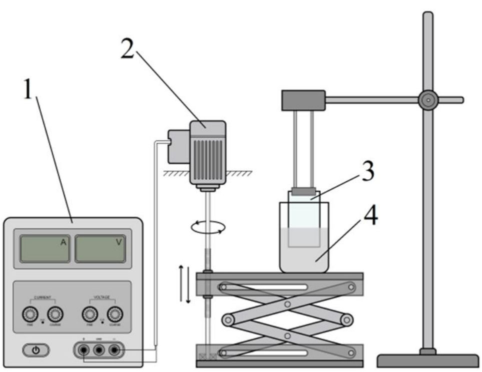


Fig. 1. The scheme of the experimental setup for the TiO_2 films obtaining; 1 – Current source; 2 – Electric motor with gear; 3 – Substrate; 4 – Film-forming solution.

The proposed design makes it possible to achieve a uniform drawing of the substrate and to vary the drawing rate within a fairly wide range.

The process of coatings obtaining was as follows:

At the first stage, a solution of titanium isopropoxide in isopropyl alcohol was prepared. Then the substrate was immersed in the solution, after which it was pulled out at the rate of 1 to 10 mm / min. For the growth of films with the desired thickness, the operation of dip-coating was performed several times.

Cylindrical washers of diameter ~ 5 mm and thickness ~ 2 mm, made of titanium alloy (VT-6) were used as substrates.

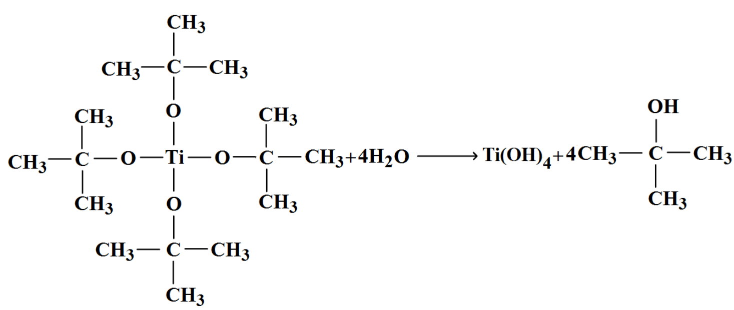
2.2 Studying of the titanium dioxide coatings morphology

Morphology of the TiO_2 coatings was studied by scanning electron microscopy using the scanning electron microscope "MIRA-LMH" with the element determination system AZtecEnergy Standart / X-max 20 (standard) ("Tescan", Czech Republic) with an acceleration voltage of 10 kV.

3 Results and discussion

Reaction for the titanium oxide film obtaining can be described by the following equations:

In air, when interacting with water vapor, hydrolysis of titanium isopropoxide occurs:



On calcination of the obtained titanium hydroxide film, titanium oxide is formed:

$$Ti(OH)_4 \xrightarrow{400^oC} TiO_2 + 2H_2O\uparrow$$

All the TiO_2 films obtained were calcined at a temperature of 400 °C.

Since the growth of the film occurs during the crystallization of titanium hydroxide from titanium isopropoxide in air containing water vapor, such factors as substrate roughness, air humidity, the concentration of titanium isopropoxide in solution, the rate of substrate drawing and the presence of additional crystallization centers have a pronounced effect on the films growth rate [12], therefore, the greatest attention should be paid to these factors.

Within the framework of the study, TiO_2 coatings were obtained via manually drawing the substrate from the solution at a relatively high rate of 30 mm / min and by automated drawing from the solution at low drawing rates (1 to 10 mm / min).

Fig. 2 shows the micrographs of the BT-6 substrate prior to coating.

The substrate is quite rough, which can cause an increase in the titanium hydroxide crystallization rate and the formation of additional crystallization centers, which can lead to deterioration in the coating quality.

Fig. 3 shows SEM-micrographs of TiO_2 coatings obtained via manually drawing the substrate from the solution.

The photographs show that the film contains microparticles of titanium oxide, formed due to rapid crystallization. Using ×3000 zoom, it can be seen that fissures are present in the film.

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The formation of fissures is caused by the difference in the thermal expansion coefficient of the substrate and film material, as well as by the imperfection of the film structure.

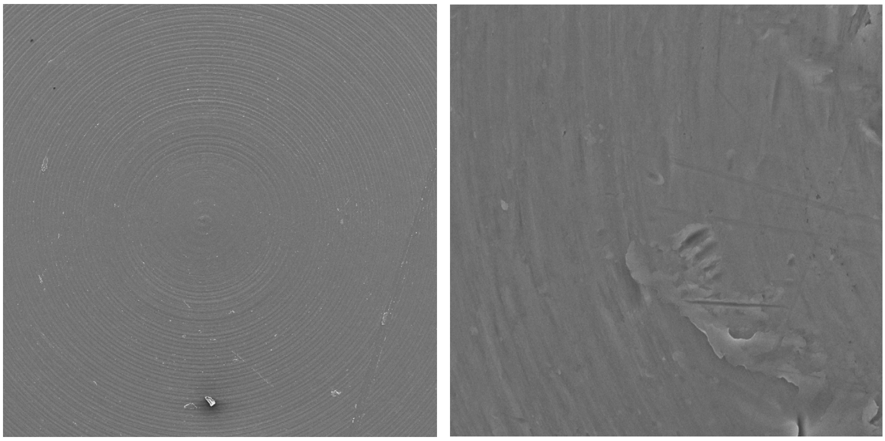

Fig. 2. SEM-micrographs of the BT-6 substrate

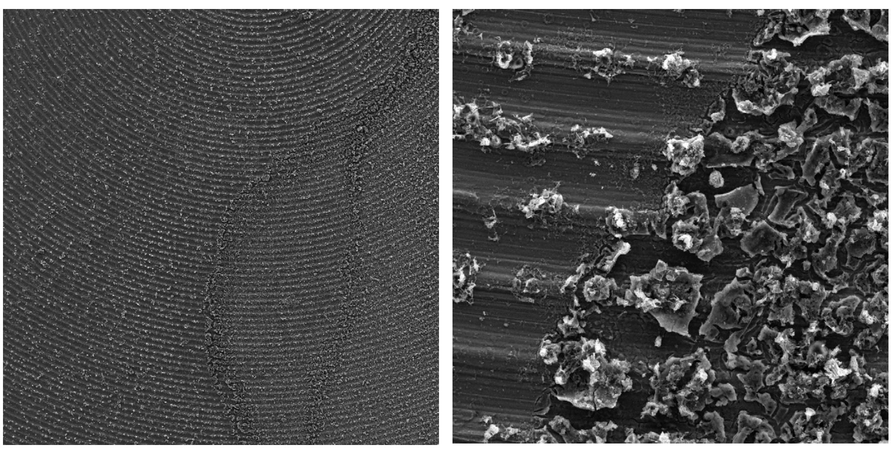

Fig. 3. SEM-micrographs of TiO_2 coatings obtained via manually drawing the substrate from the solution

Figs. 4-5 show SEM-microphotographs of TiO_2 coatings obtained by automated drawing of substrates from a solution at different rates.

Analysis of microphotographs showed that the surface morphology of the coatings obtained at lower drawing rates by an automated method is much more homogeneous – the titanium dioxide film completely repeats the topography of the substrate surface, there are almost no fissures. There is an insignificant amount of titanium dioxide microparticles (Fig. 4) at a drawing rate of 2 mm / min. At a drawing rate of 7 mm / min, TiO_2 microparticles on the surface are practically absent.

Due to the absence of defects and fissures, these coatings can be used in the field of implantology to improve the biocompatibility of implants, since the implant material is completely shielded from the biological environment by a titanium dioxide film in this case.

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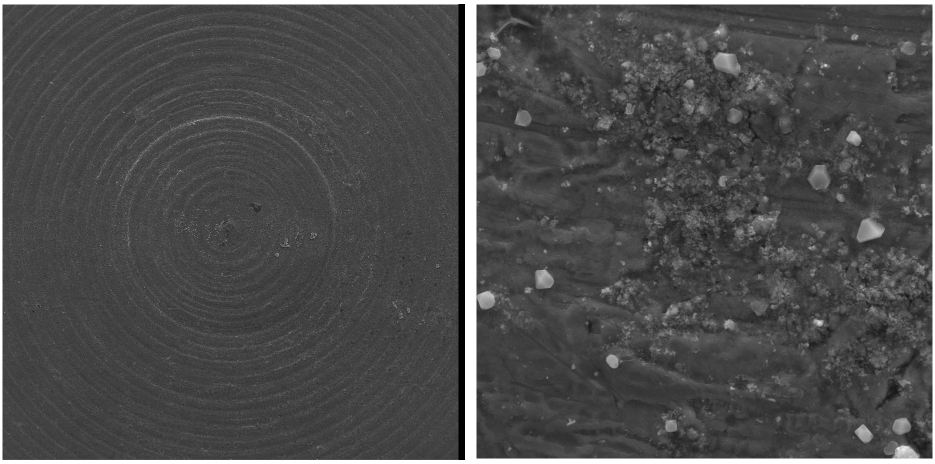

Fig. 4. SEM-micrographs of TiO_2 coatings obtained by automated drawing of substrate from the solution (2 mm / min)

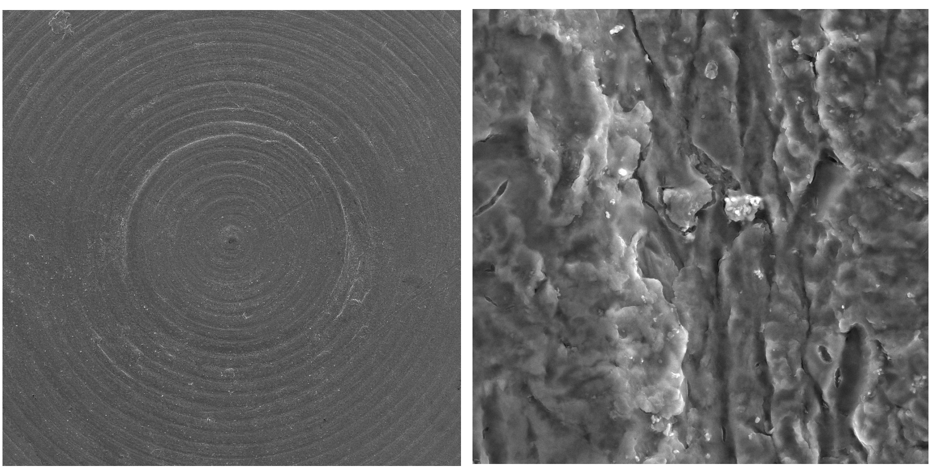

Fig. 5. SEM-micrographs of TiO_2 coatings obtained by automated drawing of substrate from the solution (7 mm / min)

Conclusions

The obtained data shows that the presented dip-coating method allows obtaining of high-quality titanium dioxide coatings that completely repeat the substrate surface relief. The coatings morphology is significantly influenced by such factors as the substrate drawing rate and the relief of the substrate surface. Selection of the substrate drawing rate allows reducing the influence of the surface topography and avoiding the occurrence of crystallization centers, and as a consequence, the appearance of defects in the coatings morphology, such as fissures or individual microparticles.

To obtain biocompatible coatings by this method, further research is needed to determine the dependence of the surface morphology on the conditions of their synthesis. To apply these coatings in the medical implants producing, it is necessary to conduct studies on the biocompatibility of TiO_2 coatings both in vitro and in vivo.

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