Prospects For Appliance Of Zinc Oxide Nanofilms For Dental Implants

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Abstract— The technologies used in the production of dental implants are rapidly evolving. Demand for implants is projected to increase by 39% by the year 2050. But the survival rate of modern dental implants is estimated to be 90-96%. The reason for this, in addition to bacteria, is the corrosion of the material from which the implant is made. Dental implants are exposed to water, agressive environments, which leads to the degradation of their material due to corrosion. In modern dentistry, implants made of titanium alloys are used, which contain both alloying elements and technological impurities. This leads to their release and cause inflammation of the bone in which they are implanted. A promising direction for improving implant is the application of coatings on titanium dental implants. One of the promising coatings is zinc oxide. The advantages of this material include its strength, bactericidal, high biocompatibility, availability.

Another important factor is the wetting of the surface, which affects the interaction with the liquid environment in the oral cavity and affects the implant's viability.

The aim of our research was to apply a simple sol-gel coating technology of zinc oxide, which does not require expensive equipment and can create a nanocoating with a thickness of 5-10 nm, as well as to study the wettability of the developed nanocoating.

The idea of the work wasthat sol-gel technology will allow to determine the optimal thickness of zinc oxide nanocoating, which will comprehensively provide both antibacterial properties and hydrophilicity of the coated implant.

It was experimentally established that the best wetting is observed at a thickness of zinc oxide coating of 5-10 nm. For titanium implants, it is possible to recommend applying a zinc oxide coating of 5-10 nm using sol-gel technology.

Keywords—dental implant; wetting; nanocoating; zinc oxide

I. INTRODUCTION

Technologies used in the manufacture of dental implants are rapidly advancing. According to expert estimates, the demand for implants is expected to increase by 39% by 2050 [1]. However, the success rate of modern dental implants is estimated to be 90-96% [2]. Besides bacteria, corrosion of the implant material is also a concern. An ideal material for dental implants should be non-toxic, biocompatible, corrosion-resistant, sufficiently strong, and affordable. Dental implants are exposed to water, alkalis, acids, cold and hot environments, which contribute to material degradation through corrosion. Therefore, modern dentistry utilizes implants made of titanium alloys, which contain both alloying elements and technological impurities. This leads to their release and can cause inflammation of the surrounding bone tissue. Recently, one promising direction for improving implant success rates is the application of coatings on titanium dental implants [3].

One of most used coatings is titanum oxide [4]. It can be deposited by electrochemical anodization. Implant as anode with Ti/Pt cathode is immersed into electrolyte with appliance suitable voltage. This leads to forming epitaxial film on implant’s surface. Such implants have good mechanical strength and stability, its nanopourus have perfect size for fast osteointegration. This deposition technique is easy and cheap, but produced in it implants contribute advanced conditions to bacteries grow. It can leads to peri-implantitis.

Another coat is hydroxyapatite [5]. It’s not toxic and non-immunogenic. Nowtime methods for its deposition, such as electrochemical deposition, electrophoretic deposition and electrospray deposition leted obtain advanced biocompability, osteogeneration and antibacterial properties. By its structure it likes to tooth enamel that leads to better non-immunogenic. But deposition methods for this coat are difficult and expensive. They need expensive special equipment.

Polymeric layers are new strategy of implants improving [3]. Most common using coatings are chitosan cellulose and silk fibroin-based nanomaterials. Chitosan is widely used to tissue engineering and controlled drug delivery. It is known by its antimicrobial properties and high biocompability. But resent studies [6] show toxicity its nanoparticles.

One of the promising coatings is zinc oxide. This material is strong, bactericidal, biocompatible with human tissues, and is even used in medical preparations, ointments to accelerate wound healing, and cosmetics as powdered additives to creams, etc. [7]. In dentistry, zinc oxide powder is used in filling materials. Among the advantages of this material, its low cost and availability of raw materials can also be mentioned. In the work [3, 8], data on its potential as an antibacterial coating for dental implants are provided, even with a coating thickness of 1-10 nm, applied by vacuum spraying. But this work did not address the issue of wettability, although it is known that zinc oxide can have hydrophobic properties[9]. At the same time, it is known that the properties of nanoscale materials can significantly differ from bulk materials. The wettability of the implant surface affects its interaction with the biological environment and, accordingly, the implant's success [10]. A hydrophilic surface issuitable for blood coagulation in comparison with a hydrophobic surface. Therefore, dental implants manufactured with highly hydrophilic and rough implant surfaces are more favorable for osteointegration in comparison with the conventional ones. Hydrophilic properties are affected by the chemical composition of the dental implant. Overall, hydrophilic surfaces are considered ideal surfaces in comparison with hydrophobic surfaces in light of their interactions with cells, tissues and biological fluids.

The wettability of ZnO films can be controlled [11, 12], which is important not only in sensing for investigating liquid environments but also in other areas where ZnO can be used as protective coatings with low friction [13-15].

The hydrophobicity of a material is determined by its ability to repel water. Various methods exist for measuring the hydrophobicity of materials. Here are some of them:

Contact angle (wettability angle): This method measures the angle between the material surface and a water droplet placed on it. A large angle indicates high hydrophobicity.

Water droplet method: Water droplets are applied to the material surface, and it is determined whether they bead up or spread out.

Weight method: The change in mass of the material before and after interaction with a humid environment is measured. If the mass changes only slightly, it may indicate hydrophobicity.

Electrical methods: These are based on changes in electrical conductivity or capacitance of the material upon interaction with moisture.

Impedance spectroscopy: The impedance of the material is analyzed at different frequencies, which can provide information about its hydrophobicity.

Light scattering method: Changes in scattered light upon wetting the material are measured, which is also related to its hydrophobicity.

The choice of a specific method depends on the characteristics of the material and the research requirements. Typically, a combination of different methods is used to obtain comprehensive information about hydrophobicity.

Surfaces that are highly hydrophilic compared to hydrophobic ones have better interactions with biological molecules and cells. Moreover, a hydrophilic surface promotes faster blood coagulation. Thus, dental implants with highly hydrophilic and rough surfaces are more favorable for osseointegration compared to conventional ones.

The aim of our research was to apply a simple sol-gel technology for coating with zinc oxide, which does not require expensive equipment and can create nanocoatings with a thickness of 5-10 nm.

Sol-gel technology is simple and does not require special expensive equipment, only a muffle furnace.

The idea of the work was that the application of sol-gel technology would allow determining the optimal thickness of zinc oxide nanocoating, which would comprehensively provide both antibacterial properties and sufficient strength and hydrophilicity of the coated implant.

II. MATERIALS AND METHODS

Surface hydrophilicity can be determined using the contact angle, which forms between the surface and a droplet of liquid placed on it. This method is well-suited for zinc oxide films [9]. If the droplet is placed on a surface that easily interacts with water (hydrophilic surface), the contact angle will be relatively small. In the case of a hydrophobic surface (a surface that does not interact with water), the contact angle will be quite large.

The contact angle is the angle formed between the surface of a solid and a liquid droplet placed on it. It indicates how well the liquid wets the surface. If the droplet is placed on a smooth, flat surface, the contact angle may be small. However, if the surface is rough or has irregularities, the droplet may more or less adhere to this surface.

The theory of contact angle is based on the equilibrium between the surface of the solid, the liquid, and the gas phase around them [16]. Two main models for understanding the contact angle are the Wenzel equation and the Cassie equation.

Wenzel Equation:

The Wenzel equation describes the situation when the liquid completely wets the surface of the solid. It is used for rough, porous, or uneven surfaces. The Wenzel equation is formulated as follows:

$$\cos(\theta_W)=r\cos(\theta)$$

where: θ_W- contact angle according to the Wenzel equation,

θ - contact angle on a flat surface,

r - roughness factor of the surface (the ratio of the real surface area to the horizontal area).

Cassie Equation:

The Cassie equation describes the situation when the liquid does not completely wet the surface of the solid due to the presence of surface roughness. It is used for surfaces that have texture or micro-irregularities. The Cassie equation is formulated as follows:

$$\cos(\theta_C)=f\cdot\cos(\theta)+(1-f)$$

where: θC - contact angle according to the Cassie equation,

f - Cassie factor (the ratio of the hydrophobic surface area to the total surface area).

The Cassie and Wenzel equations are used to understand the interaction of liquid with the surface of a solid and can be applied to various materials and conditions.

For the deposition of zinc oxide onto samples, representing substrates (25×25×1 mm) made of microscopic glass of "Voles" brand, the sol-gel technology was employed [17]. For this purpose, 2.2 mg of zinc acetate was dissolved in 50 ml of isopropyl alcohol and stirred using a magnetic stirrer at a temperature of 50 - 60°C for 30 minutes. As a stabilizer, 0.6 ml of monoethanolamine was added. This resulted in a colloidal solution of the sol type. The obtained solution was left at room temperature for 24 hours to form a gel. Samples were placed in a centrifuge, and the synthesized gel was applied onto the glass surface using a pipette dispenser. The samples were dried with the centrifuge spinning at a frequency of 100 rpm and simultaneous airflow at a temperature of 70°C [18]. The dried samples were annealed in a muffle furnace for 30 minutes at a temperature of 300°C to remove residual solvent, followed by another hour at a temperature of 500°C to form a zinc oxide film. As a result, a series of samples with different numbers of layers – and thus different thicknesses of the deposited ZnO film – were obtained.

The spectra of optical transmission of the samples were measured using the Mapada instruments UV 1600 spectrophotometer. The measurement range was set to 300-500 nm, which is optimal for the investigation of samples of this type and determination of the ZnO absorption threshold [19].

The visual appearance and dimensions of droplets on the samples were recorded with a digital camera in macro mode. Images were captured from the top view, after which a mask was created using software to establish the area of the droplet in pixels. Similarly, the side view was captured, and the height and radius of the droplet were measured using software. Since the sample was in a fixed position relative to the camera, the dimensions in pixels were converted into millimeters according to established standards.

The hydrophilic properties of ZnO films on Ti were also investigated. For this purpose, Ti-22 titanium grade was used, which contains 87% titanium, 6% aluminum, 5% vanadium, 1% cobalt, and possible other impurities in insignificant quantities. The ZnO film deposition process was repeated twice. Initially, the Ti-22 ingot was used without additional treatment. In the second deposition, the ingot was polished on both sides using 1000 and 2000 grit grinding wheels. Consequently, the deposited film was removed, and the surface became smoother. Subsequently, the ZnO film was reapplied using sol-gel technology. The influence of all temperature regimes during the deposition process was identical for both sides, whether coated or uncoated.

III. RESULTS AND DISCUSSION

Using the obtained spectra, a comparison of the thicknesses of the deposited films was conducted for some samples, as shown in Fig. 1.

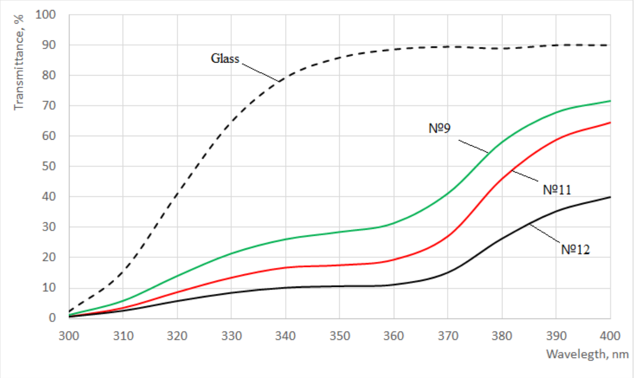


Fig. 1. Transmission spectra of samples No. 9, 11, and 12 compared to the original "Voles" glass.

The transmittance coefficient was compared at a wavelength of 350 nm, where the influence of the ZnO film is most significant.

With a droplet volume of 20 μl, from the top view, it maintained a spherical shape for all samples except for the clean glass and samples with the thinnest films (thickness measured using AFM), 5 and 20 nm. The area of the droplets ranged from 10 to 26 mm2.

In addition to distilled water, droplets of the same volume were applied with a physical solution. A comparison of the droplet areas is presented in Fig. 2.

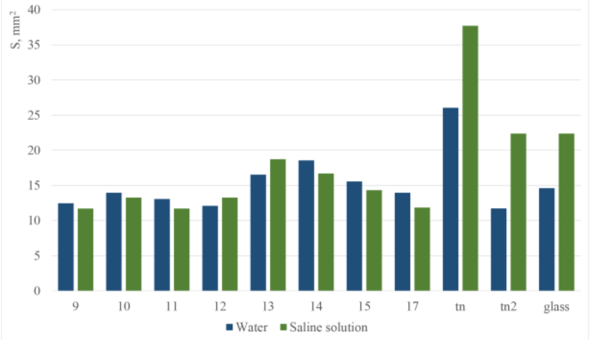


Fig. 2. Comparison of the droplet areas of water and the physical solution, where:tn - sample with a ZnO film thickness of 5 nm, tn2 - sample with a ZnO film thickness of 20 nm, glass – cleansubstrate "Voles" glass.

The area of water and physical solution droplets compared to the transmittance coefficient at a wavelength of 350 nm is presented in Table 1.

TABLE I. DROPLET AREA RELATIVE TO THE TRANSMITTANCE COEFFICIENT AT A WAVELENGTH OF 350 NM.

Sample Name	**Water Droplet Area, mm^2**	**Physical Solution Droplet Area, mm^2**	**Transmittance Coefficient T, %**
9	12,46	11,71	38,2
10	13,97	13,28	85,7
11	13,08	11,71	17,6
12	12,09	13,28	49,8
13	16,53	18,74	85
14	18,56	16,71	79,5
15	15,56	14,33	87
17	13,97	11,85	75,9
tn	26,05	37,71	86
tn2	11,73	22,39	86
glass	14,62	22,39	86

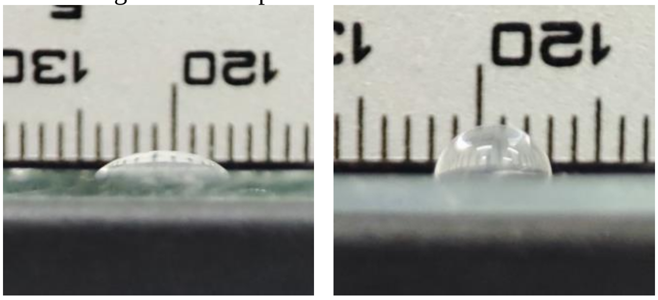
For samples 9 - 17, the area of droplets directly does not depend on the transmittance coefficient (film thickness accordingly), and the area of droplets of the solution is slightly smaller than the droplets of deionized water. For samples with ultrathin films and pure glass, the area of the solution droplet is about 50% larger than the droplet of pure water. Particularly noteworthy is sample tn3 with a film thickness of ~5 nm, for which the area of water and solution droplets is larger than that of the original glass by 56% and 59%, respectively, indicating a strong surface hydrophilicity. To exclude the influence of changing the shape of the formed droplets on the surface, these samples were re-measured with droplets of 10 μL. The droplets' shape was spherical, and the previously measured ratios were preserved.

The droplet shapes when viewed from the side, from which the contact angle was calculated using formula 1, are shown in Fig. 3.

Assuming the droplet forms a hemisphere, then the contact angle can be found using the following formula:

$$\cos\theta = \frac{r}{\sqrt{r^2 + h^2}}$$

where:
θ - contact angle (wetting angle),
r – radius of the droplet,
h – height of the droplet.



a b

Fig. 3. Droplets of distilled water with a volume of 20 µL formed on (a) clean glass of "Voles" brand and (b) sample 12.

As can be seen from Fig. 3, the original glass exhibits significantly greater hydrophilicity than the samples with ZnO films. To calculate the contact angle, as in previous measurements on clean glass and samples with ultrathin films tn and tn2, droplets with a volume of 10 µL were also measured. The calculated contact angles are presented in Fig. 4.

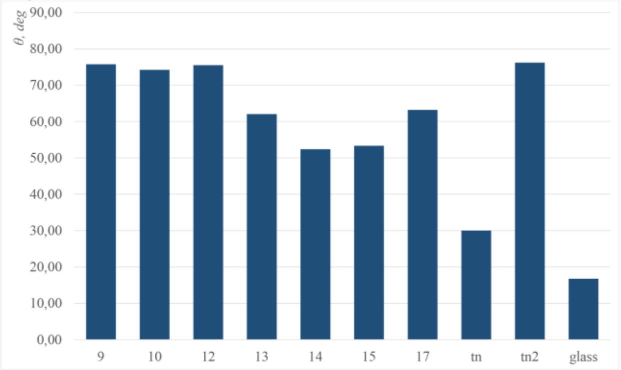


Fig. 4. Contact angle of droplets of distilled water with a volume of 20 µL.

As a result, the contact angle of the original glass used as the substrate amounted to 16.8°, indicating strong surface hydrophilicity. Application of ZnO films reduces the hydrophilicity to angles close to 90°. Particularly interesting results were obtained for thin films of 5 and 20 nm, where it is evident that the surface structure of the substrate itself has a significantly greater influence on the ZnO film surface.

Additionally, when the samples are positioned at an angle, the influence of surface hydrophilicity on the droplet shape can be observed as it spreads, as shown in Figure 5.

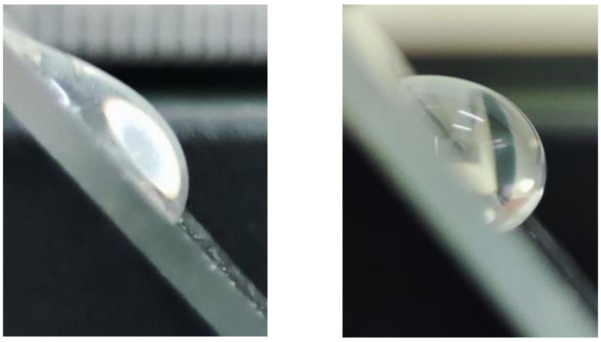


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Fig. 5. Droplet rolling on the surface of samples at an angle of approximately 45°, where (a) is clean glass of "Volles" brand and (b) is a sample with ZnO film 12.

As can be seen from Figure 5, for samples with applied ZnO films, the difference between the advancing and receding angles of the rolling droplet is small, less than 20°, and the droplets firmly adhere to the surface, which may indicate the "rose petal effect" described in [9] and characteristic of hydrophobic surfaces.

Overall, the application of nanofilms <200 nm allows even superhydrophilic surfaces to transition to hydrophobic ones, which can be useful in many fields of application. With ultrathin films less than <20 nm, it is possible to retain the surface's hydrophilic properties, which in turn can be beneficial when using ZnO films as protective coatings for various sensors. By changing the thickness of the ZnO films, which can be effectively achieved by varying the number of layers applied using the sol-gel method, it is possible to regulate the surface's hydrophilicity. Also promising is the doping of such films, which can significantly alter the surface structure, thereby changing its hydro properties.

During the investigation of the hydrophilic properties of the ZnO film on Ti-22, droplets of deionized water were applied in volumes of up to 20 µL. However, due to the high hydrophilicity of the titanium alloy Ti-22, droplets of large volume did not maintain their shape. Droplets with volumes of 5 and 10 µL retained their shape and allowed measurements of their spatial dimensions in profile. The results of the contact angle calculation are presented in Fig. 6 and 7.

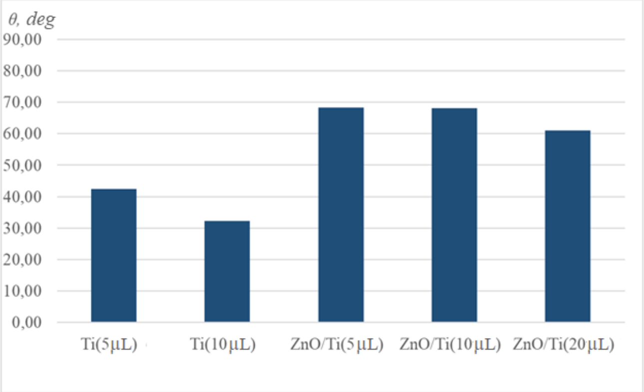

Fig. 6. Contact angle for the sample before grinding

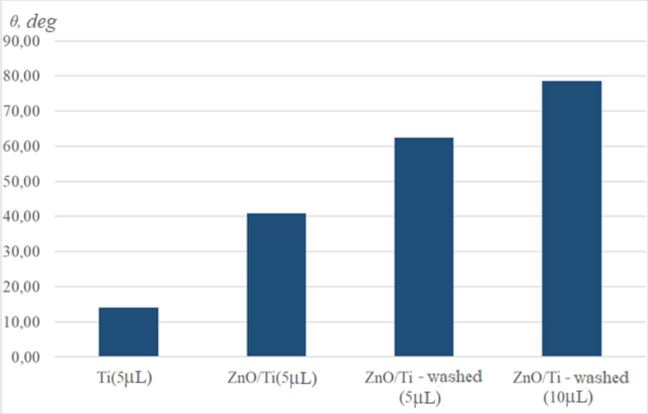

Fig. 7. Contact angle for the sample after grinding

As evident from the provided figures, Ti-22 exhibits high hydrophilicity after grinding ($\theta = 14°$). The application of ZnO film reduces its hydrophilicity; however, the surface still remains hydrophilic ($\theta < 90°$). It is also worth noting that the applied ZnO films are quite thick; therefore, as indicated by previous results, reducing their thickness can mitigate this effect and consequently achieve a more hydrophilic surface.

During the measurements on the sample after grinding, the results were also compared without rinsing the applied ZnO film. Its hydrophilicity was higher, which may be attributed to the residues of unreacted components of the sol-gel.

Due to the high hydrophilicity, the contact angle is most accurately measured with droplets of 5 µL volume. Droplets of larger volume begin to lose their shape on samples with higher hydrophilicity. Therefore, the best comparison of the contact angle of droplets is with a volume of 5 µL (Fig. 8).

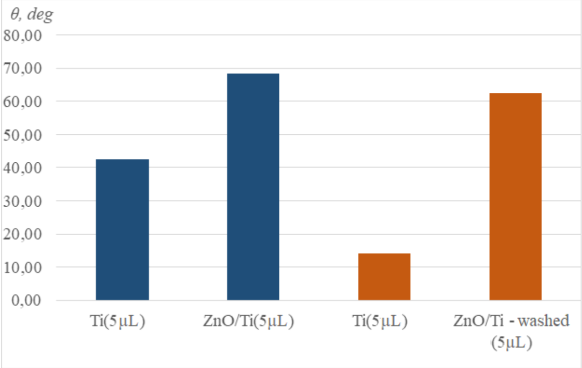

Fig. 8. Contact angle of 5 µL droplets of deionized water.

After grinding, the surface of Ti-22 became significantly more hydrophilic, with the contact angle (θ) decreasing by 28.3°. This change in surface properties is reflected in the hydrophilic properties of the side with the applied ZnO film, albeit to a lesser extent, with θ decreasing by only 5.9°. Nevertheless, it remains a hydrophilic surface since θ is significantly less than 90°.

IV. CONCLUSION

Experimentally, it has been established that the best wetting is observed with a zinc oxide coating thickness of 5-10 nm. Therefore, for titanium implants, the application of a zinc oxide coating of 5-10 nm using sol-gel technology is recommended.

The application of ZnO films onto the surface of Ti-22 using sol-gel technology reduces the surface hydrophilicity, as evidenced by the increase in contact angle (θ) by 26° on the rough surface without grinding and by 48.4° on the polished surface. Overall, the influence of surface roughness on the hydrophilic properties of Ti-22 is significant, albeit to a lesser extent on the surface with the applied ZnO film. It can be assumed that deposited by sol-gel ZnO fills in surface irregularities, thus smoothing it out. Additionally, reducing the thickness of the film on a smoother surface will better preserve the hydrophilic properties of Ti-22.

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