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A study on the physicochemical properties of surface modified Ti13Nb13Zr alloy for skeletal implants

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As it is widely stated in the literature, biofilms are responsible for most chronic infections, which have grown exponentially over the past three decades. The use of so-called alloys, as a new generation of materials, enables us to find the golden mean in the arena widely known as implantology. The use of the surface layer, using the chosen Atomic Layer Deposition method, is to be the basis for minimizing the risk of an organism reactions. Therefore, the primary objective of this study was to observe the impact of physicochemical properties of the surface layers (bactericidal) on the processes that occur on the implants surface made of titanium biomaterials used in bone structures. The study also attempted to evaluate the physicochemical properties of the ZnO coatings, deposited on the substrate of one of the new generation Ti13Nb13Zr alloys, using the ALD method. Included in the assessment of the physicochemical properties of the surface layers formed in this manner, we perform pitting corrosion resistance tests, scratch tests, tribological tests and surface wettability tests. Based on the obtained data, the differing physicochemical properties of the alloy with ZnO coatings are found to be dependent on the applied surface modification. For the conducted tests, differences are determined for the tests on the corrosion resistance, surface wettability and the abrasion resistance for samples with and without the ZnO coating. In addition, tests show that the coating applied to the alloy, which is previously subjected to the sand-blasted process, is characterized by improved adhesion.

Key words: *biomaterials, ALD method, surface modification, skeletal system*

1. Introduction

The problems caused by microorganisms is quite common and the pathway of the penetration of bacteria is varied. The formation of individual bacteria is not dangerous, but biofilms as a cluster can be hazardous. Bacteria may exist in the planktonic form (a collection of dispersed bacterial cells) or in the form of a biofilm, as a three-dimensional, organized structure that contains bacteria which is surrounded by a matrix composed mainly of sugar and protein polymers [5], [7], [16], [25]. Reducing the possibility of biofilm formation and the development on the surface of implants are two of the basic research problems that exists that prevents microbial growth [19]. The use of numerous modifications, related to surface treatment, minimizes bacterial colonization [18]. Titanium alloys are used in the broadly known field of long-term implantology [3], [22], [24], however, due to the effects of disturbing the durability of the connection between the implant and the bone, modifications can be made to extend the life of the implant [18]. The antibacterial properties of ZnO are related to its effects on proteins and the proliferation of fibroblasts [18], [21].

By improving the biocompatibility, a simultaneous increase in the corrosion resistance and a reduction in biofilm adhesion are achieved. New strategies for evaluating tin oxide functional materials are of fundamental importance for the development of new biomaterial surfaces. This is one of the most promis-

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ing materials due to its excellent physical properties. The methods for applying modified top coats must ensure repeatability and homogeneity of their physical and chemical properties [9], [12], [18], [20], [33]. The structure and chemical composition of the implant coating can be modified using various methods, among which are the dominantly employed methods known as PVD and sol–gel [11], [14], [18]. One of the most important aspects in relation to implants is to ensure a consistency for the geometric features along their entire length, which the above-mentioned modifications are not able to provide. Therefore, in this context, an unrivaled efficient modification of the surface involves the application of coatings using the ALD (Atomic Layer Deposition) method [1], [4], [8], [10], [13], [34].

Outside of the improvement of the biocompatibility, an important issue relates to the production of layers using the appropriate set of their mechanical properties [25]. ZnO coatings [20], [26], [27] are used in many industrial applications due to their electrical, optical and electrochemical properties, and also their high chemical stability [15], [28]. In addition, they can be used as coatings in biomedical devices because of their antimicrobial effect and high biocompatibility. So far, for such applications, researchers have attempted to produce reinforcing fillers for biopolymer implants, such as scaffolds in tissue engineering [8], [30]. The biocidal activity of such structures, against gram-positive *S. aureus* and gram-negative *E. coli* bacteria, and their non-toxicity has been demonstrated [29]. Similar observations were noted by Yang et al. [31], who showed that a TiO_2 layer formed by an ALD method on the surface of the material could improve its surface wettability and its mechanical properties, such as wear-resistance and surface hardness, which can enhance the performance of this polymer. Such surface improvements decrease the microbial adherence and biofilm formation on the surface, which is essential in biomedical applications. Improving the wettability of the titanium alloy implants with TiO_2 by the use of the ALD method is beneficial with respect to the increased cellular attachments alongside a reduced biofilm adherence.

In another study by Basiaga et al. [23], TiO_2 was deposited by the ALD procedure on two grades of Ti alloys using $TiCl_4$ and water. Based on their results, the surface corrosion resistance was improved by increasing the thickness of the film. Moreover, the greatest amount of film adhesion was achieved at 1250 ALD cycles, regardless of the substrate types. However, no significant difference in the wettability and surface topography was obtained by varying the number of cycles [8]. In a study by Patel et al. [17], a thin film of TiO_2 was deposited on the Ti alloy (Grade V) (Ti-6Al-4V) substrates using Tetrakis (diethylamino) titanium (TDEAT) and water at 250 °C. A gradual increase in the wettability was reported after each stage of the treatment, including pristine, deionized (DI) water wash, N_2 drying, sonication in methanol, ALD treatment and post-ALD DI water wash, respectively. Besides, anatase TiO_2 was obtained after 5 min N_2 post-annealing at elevated temperatures (600 and 800 °C) [12]. In addition Xiangmei Liu et al. [31], using the nanoscratch tests, showed that this hybrid coating had good bonding strength with the substrate and a similar Young's modulus to natural bone.

In vitro corrosion tests demonstrated that a thicker ZrO_2 nanofilm on the surface can reduce the corrosion rate of the Mg substrate when compared to a thinner coating. When increasing the ZrO_2 deposition cycles from 25 to 100, the corrosion resistance could be significantly increased by two or three orders of magnitude. To the best of our knowledge [25], only a few studies have reported on a ZrO_2/PLGA hybrid coating that enhances the corrosion resistance of the Mg-based alloys [31]. Therefore, the primary objective of this study is to observe the impact of the physicochemical properties of the surface layers (bactericidal) on the processes that occur on the implants surface made of titanium biomaterials used in bone structures.

2. Materials and methods

The material used in the following tests was Ti13Nb13Zr alloy. The samples, in the form of discs, were taken from rods of 14 mm in diameter. The specimens were then divided into two groups, according to the preparation of the surface as follows: POL – polishing (Ra = 12 μm) and SAND – sandblasting (Ra = 0.25 μm). For the sandblasting, quartz sand (SiO_2) of 50 μm gradation was were used, while for polishing, a SiC foil was used. The employment of various surface treatment methods resulted in the obtaining of various roughness values. Subsequently, the ZnO layer was applied to the polishing and sandblasting samples by Atomic Layer Deposition (POL_ZnO and SAND_ZnO). Diethyl zinc was used as the ZnO precursor, which reacted with deionized water, allowing for the deposition of thin films. The application process was performed at a temperature of 150 °C and 1000 cycles were used. To assess the suitability of the proposed surface modification method, we proposed a series of tests. The final stage of the proposed surface treatment involved medical sterilization, which was conducted using a steam method in a BASIC autoclave at temperature $T = 135$ °C and under a pressure $p = 2.1$ bar.

2.1. Potentiodynamic method

In the first stage, the pitting corrosion resistance tests were performed using the potentiodynamic method. The reference electrode was Ag/AgCl 3M KCl, while the auxiliary one was a platinum rod. The scan rate was set to 3 mV/s. Assays were carried out in Ringer's solution of the following chemical composition: NaCl – 8.6 g/dm^3, KCl – 0.3 g/dm^3, $CaCl_2$ $2H_2O$ – 0.33 g/dm^3, at $T = 37 \pm 1$ °C and a pH of 6.9 ± 0.2. These tests provided and helped us analyze information concerning the structural characteristics of the layers, possible defects, lack of sealing, substrate reactivity and the presence of barrier properties involving the electrolyte.

2.2. Scratch test method

In this paper, mechanical tests (like the scratch test) are used to determine the scratch resistance. The test involved creating a scratch with the use of a penetrator – i.e., a Rockwell diamond cone – with a gradual increase in the normal force loading applied to the penetrator. The tests were performed with an increased loading force from 0.03 to 30 N and using the following operating parameters: loading speed 10 N/min, table speed 1 mm/min and scratch length ~3 mm.

2.3. Tribological testing

The tribological wear test was conducted to learn about the friction, wear and surface adhesion. The abrasion tests were performed using a tribometer, with the application of a force load of 0.5 N successively on all the samples, for which the following courses of the abrasion coefficient were obtained. The steel ball with a diameter of 6 mm was used during these tests.

2.4. Wettability of surface

To determine the wettability of the surface, a contact angle method was performed on the selected samples. In order to determine the surface wettability of the selected samples, contact angles tests were performed by use of the sitting drop method and the surface free energy (SEP) by the Owens–Wendt method. Measurements of the contact angle of each surface were made using distilled water and diiodomethane of volume 1.5 ml and applying the Surftens Universal optical goniometer (OEG) and computer software Surftens 4.5 for the analysis of the recorded image of the drops. The measurements were performed at the room temperature ($T = 23 \pm 1$ °C) over 60 seconds with the sampling rate of 1 Hz. The obtained data showed the different physicochemical properties of the antibacterial films generated under surface modification.

3. Results

3.1. Potentiodynamic method

The samples, after their vibration treatment, sandblasting and polishing with the ZnO layer applied using ALD technology, were subjected to potentiodynamic tests of the resistance to the pitting corrosion in saline solution (PBS). The results of these procedures are displayed in Fig. 1 at the polarization curves. The values shown correspond to the corrosion potential (E_{corr}), polarization resistance (R_p) and current density ($WE_{(1)\mathrm{Current}}$) in Fig. 2.

An analysis of the course of the sample polarization curves indicates that the higher values for the R_p polarization resistance and an improved corrosion resistance occur for a polished sample with a layer of ZnO. This type of surface modification has an impact on the measurement parameters. The values of the parameters that relate to the corrosion resistance of the tested samples are summarized in Table 1. The values shown correspond to the corrosion potential (E_{corr}), polarization resistance (R_{p}) and current density ($WE_{(1)\mathrm{Current}}$) in Fig. 2.

Table 1. Results of potentiodynamic tests

Sample	Polarization data	
	E_{corr} [mV]	R_{p} [kΩ·cm^2]
SAND	200	110
SAND_ZnO	–190	181
POL	1880	236
POL_ZnO	–30	263

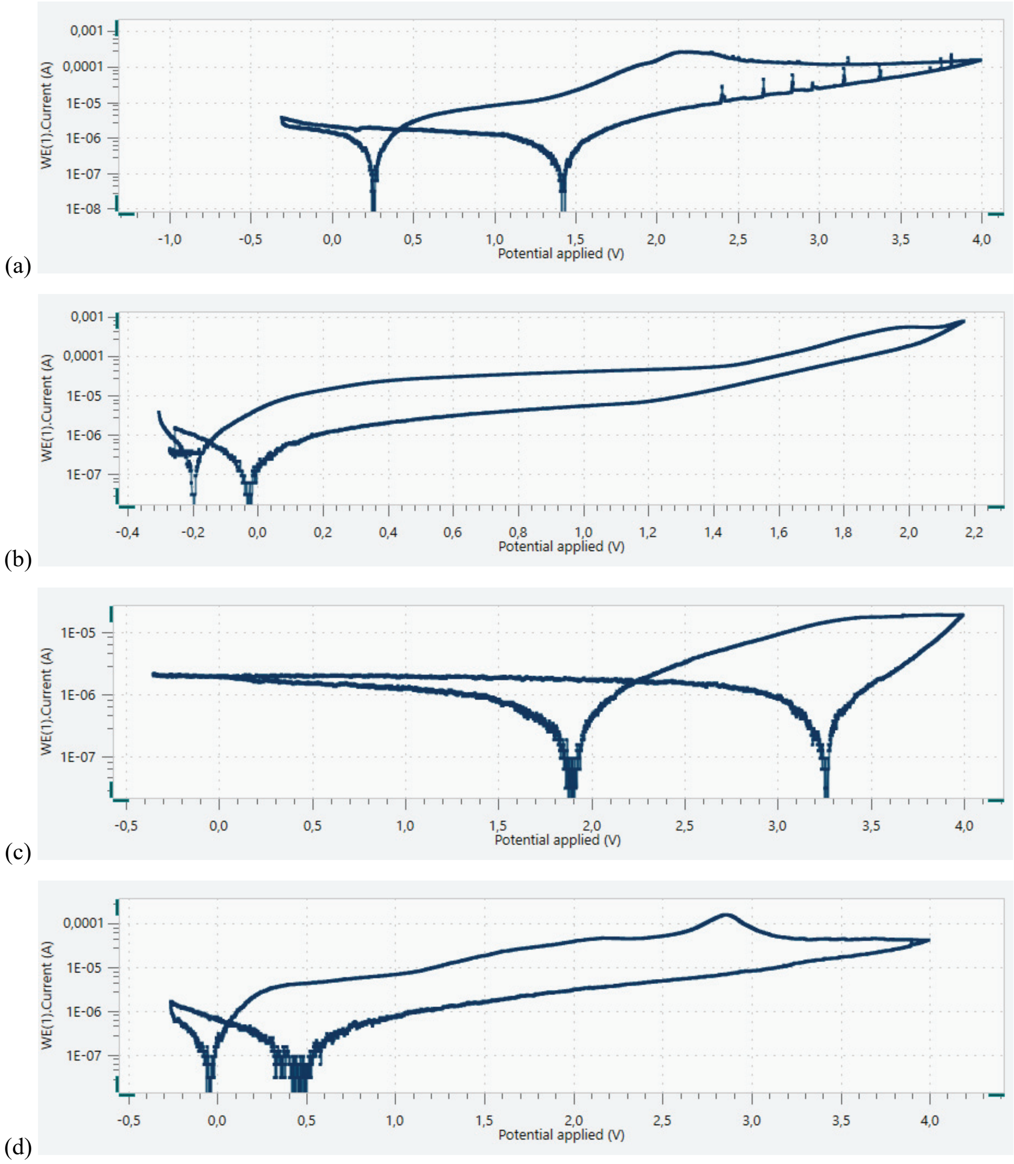

Fig. 1. Graphs showing the polarization curves for Ti13Nb13Zr after: (a) SAND, (b) SAND_ZnO, (c) POL, and (d) POL_ZnO

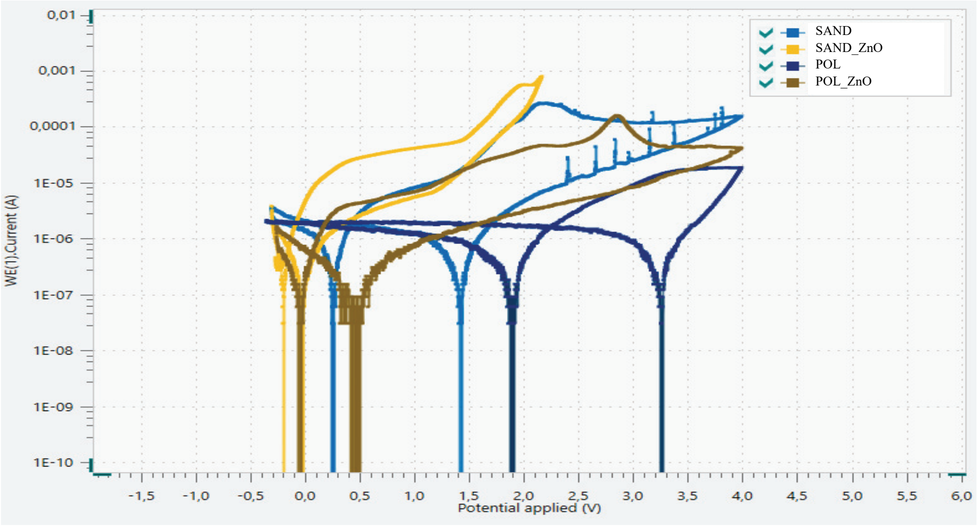

Fig. 2. Plots of the course of the corrosion potential for all samples

3.2. Scratch test

In the next stage, the scratch test was conducted. On the basis of the obtained results, the differences in the values of the critical force, which is a measure of the adhesion, were found. The values of the parameters corresponding to the results of the scratch test are summarized in Table 2.

Table 2. Results of scratch test

Method of sample surface preparation	Coating damage	Average force value *F* [N]
SAND_ALD	Chipping Lc_2	4.04
	Complete destruction of Lc_3	6.22
POL_ALD	Chipping Lc_2	–
	Complete destruction of Lc_3	2.22

Adhesion test data (Table 2) showed differences depending on the surface preparation. The sandblasted samples (SAND_ALD) had the highest adhesion. The fundamental influence of the type of surface modification on the adhesion to the substrate subjected to different types of surface modification was found. Discontinuous perforation of the coating was observed in every case analyzed. Improved adhesion was determined for the case where the coating was applied to the previously sandblasted surfaces of a titanium alloy (Figs. 3, 4). Additionally, for each of the samples, there was no acoustic emission signal, which proves that the bonding energy between the coating and the substrate was too low.

3.3. Wettability

Due to the application of the coating, a change occurred in the nature of the surface and the contact

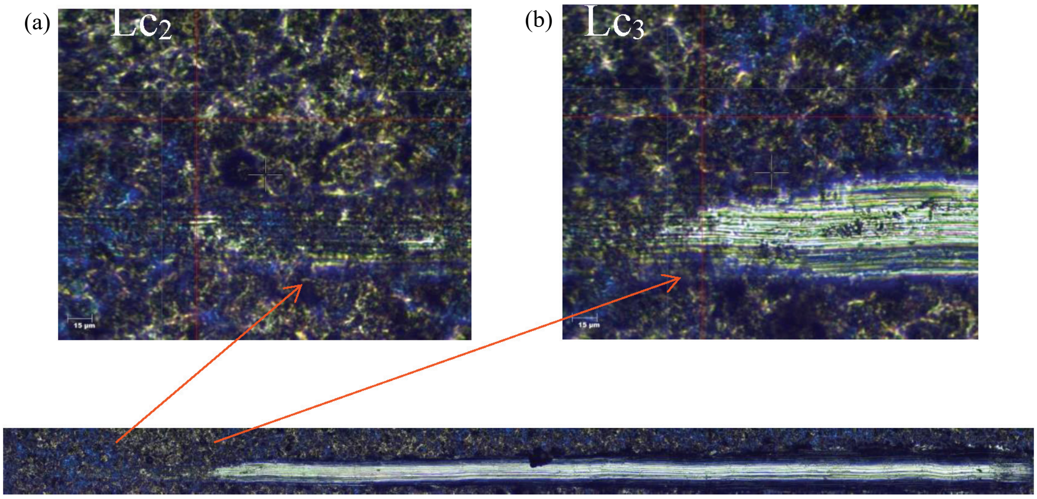

Fig. 3. Results of the adhesion tests for sandblasted samples with the ZnO coating applied

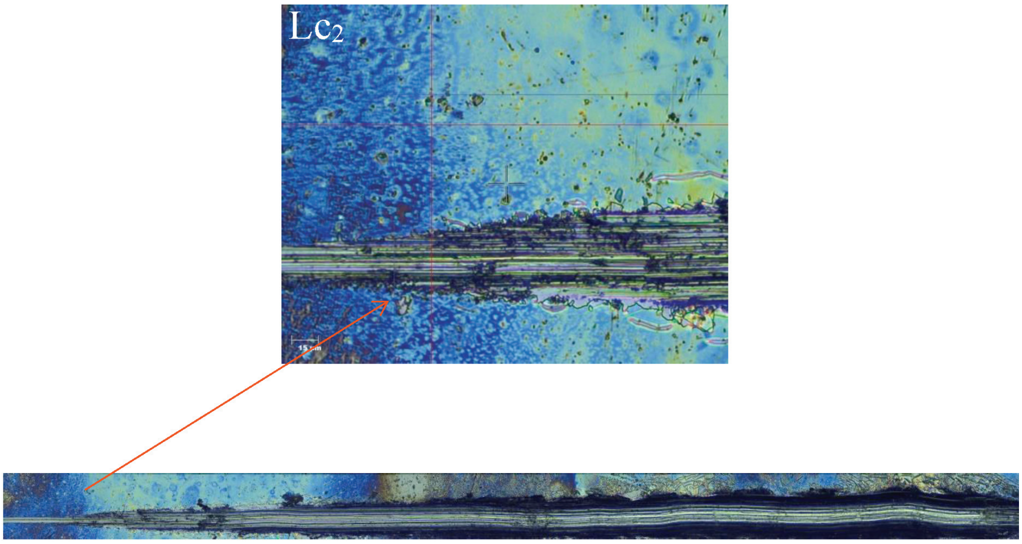

Fig. 4. Results of the adhesion tests for polished samples with the ZnO coating applied

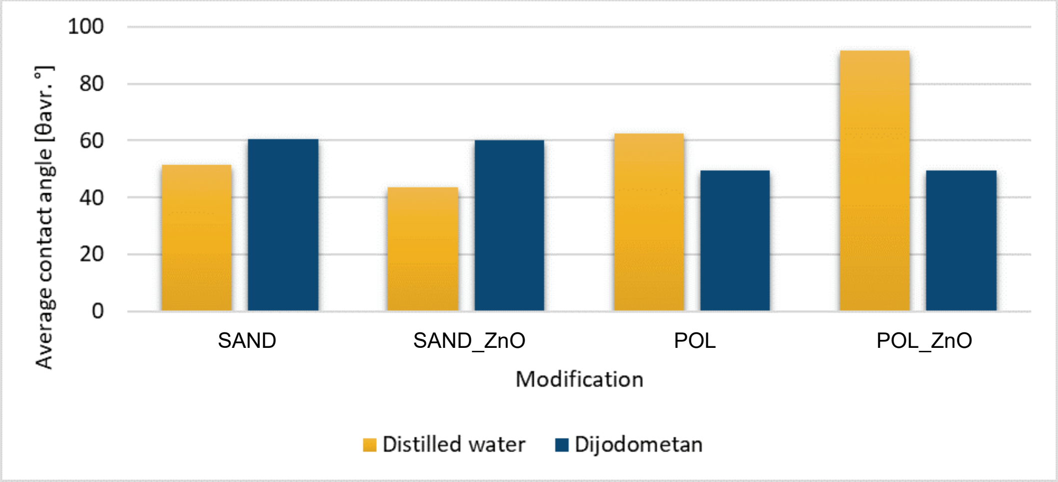

Fig. 5. Bar chart showing the average value of the contact angle of the Ti13Nb13Zr alloy samples with ZnO coating

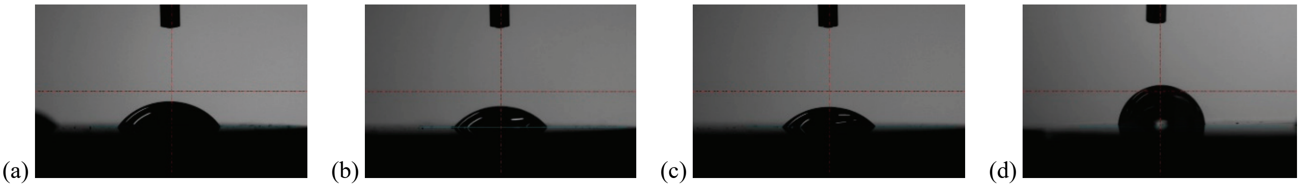

Fig. 6. Images that depict drop testing of the wettability of: (a) SAND, (b) SAND_ZnO, (c) POL, and (d) POL_ZnO

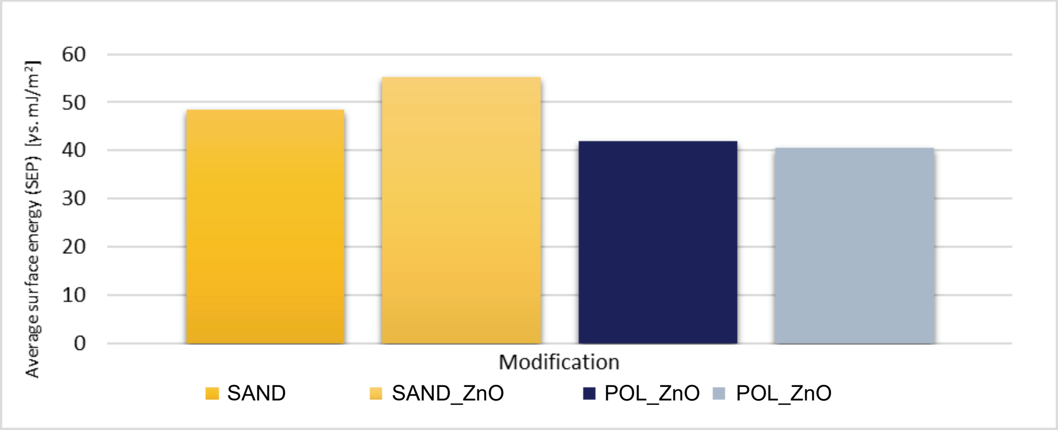

Fig. 7. Average value of the surface energy of the Ti13Nb13Zr alloy samples

angle. The average value of the contact angle for the tested samples with using distilled water and dijodometan are summarized in Fig. 5.

The noticeable difference in the contact angle values is dependent on the various properties of the liquid selected for the test. The 90° contact angle differentiates biomaterials by the adhered cells being hydrophilic or hydrophobic, which influenced the appearance of the droplets during the test, as shown in Fig. 6.

In the case of a sand-blasted surface, the coating is not changed by the character of the surface compared to the polished samples. The best option is to use a sandblasted sample with a layer of ZnO applied. The average value of the surface energy of the tested samples are summarized in Fig. 7.

3.4. Tribological testing

On application of a layer of ZnO, the coefficient of friction (Fig. 8) of the sandblasted material slightly worsened, while for polished samples, the abrasion resistance improved. Following application of the ZnO

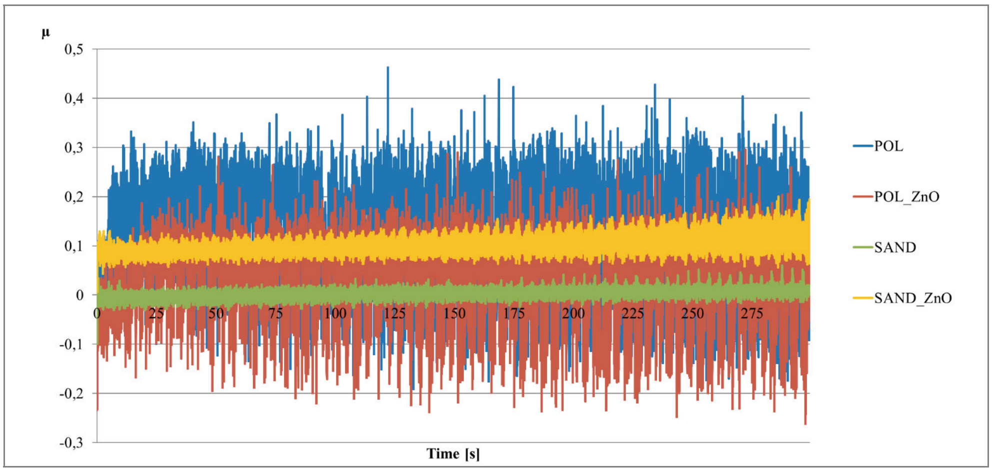

Fig. 8. Results of tribological tests

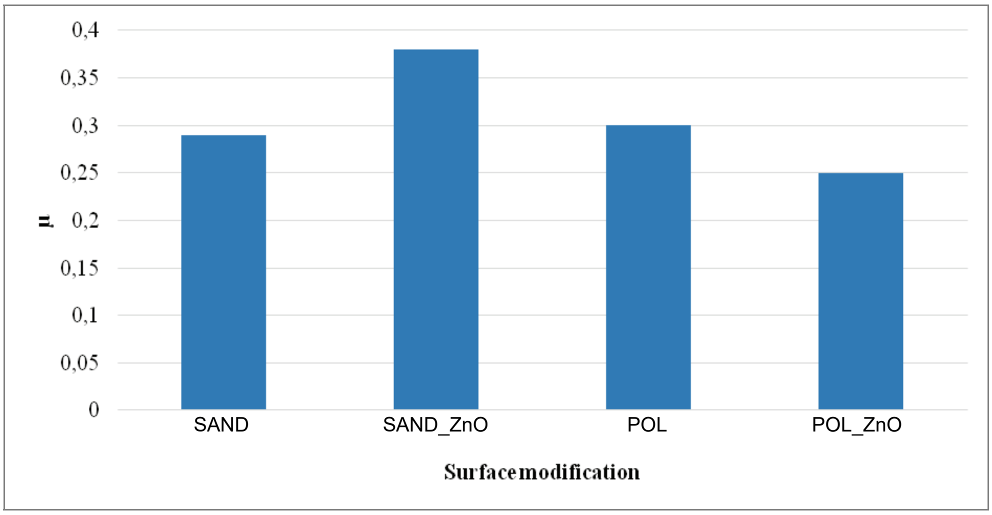

Fig. 9. Average value of the coefficient of abrasion, μ, of the Ti13Nb13Zr alloy

layer, the friction coefficient is decreased compared to the polished case.

The average value of the coefficient of the abrasion of the tested samples are summarized in Fig. 9.

4. Discussion

To improve the antibacterial properties of a Ti13Nb13Zr alloy, thus reducing the adverse effects of any bacterial biofilm formation, a modification involving the application of a ZnO coating (using the ALD method) was proposed. To ensure the required physicochemical properties of the Ti13Nb13Zr surface, certain surface treatment conditions were developed. This involved two consecutive processes: polishing and sandblasting. At a final stage, the ZnO layer was applied using an ALD procedure. The variable parameters employed included a deposition temperature of 150 °C and the number of cycles as 1000. To complete the proposed surface treatment a sterilization of the system was achieved under clinical conditions.

First, the pitting corrosion resistance was tested using the potentiodynamic method, which produced polarization curves for the analysis. Our results found that the applied ZnO coating slightly improved the electrochemical properties of the Ti13Nb13Zr alloy. In addition, more corrosion resistance was found in the samples that were previously subjected to the polishing process (Fig. 1, Table 1). As a part of the evaluation of the mechanical properties of the surface-modified Ti13Nb13Zr alloy, tests for adhesion to the substrate and abrasion resistance were performed. The obtained results showed that the applied coating is characterized by an improved adhesion for samples subjected to the sandblasting process. On the other hand, the tests on the abrasion resistance did not show any significant influence of the applied ZnO coating on the Ti13Nb13Zr alloy substrate compared to the substrate material (Fig. 8). The final stage of the research was the surface wettability assessment. For each analyzed variant, the hydrophilic nature of the surface was observed. Greater wettability, i.e., a smaller contact angle, favors the adhesion of cells to the surface of the biomaterial, which is especially important for the case of orthopedic implants, as it affects the process of integrating the implant with the tissue.

5. Conclusions

Our results directly assist the optimization of the ZnO layer creation process, using ALD-based methods, on surfaces of Ti13Nb13Zr alloy implants intended for skeletal system, thus, improving their functional properties. The obtained results may form the basis for the development of more detailed criteria on the assessment of the final quality of medical devices used in the skeletal system. More corrosion resistance was found in the samples that were previously subjected to the polishing process. The obtained results from abrasion tests showed that the applied coating is characterized by better an improved adhesion in the case offer samples subjected to the sandblasting process. For each analyzed variant during wettability tests, the hydrophilic nature of the surface was observed. Greater wettability, i.e., a smaller contact angle, favors the adhesion of cells to the surface of the biomaterial, which is especially important in for the case of orthopedic implants, as it affects the process of integrating the implant with the tissue. A comparison between different variants will ensure the required biocompatibility of the implants and contribute to minimizing the risk of post-operative complications and an improved life of the patients. The applied ZnO coating is characterized by its more favorable physical and chemical properties compared to the base material of the Ti13Nb13Zr alloy. In future work, we intend to present biological research that shows that both *E. coli* and *S. aureus* bacteria are less susceptible to the substrate with the ZnO coating.

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