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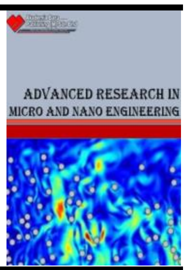

Surface Modification of Titanium Alloy by Titania/Silver Multilayers Coating for Biomedical Application

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ABSTRACT

This research aims to modify the Ti alloy by anodic oxidation to enhance its surface properties, especially corrosion resistance for biomedical applications and DC sputtering plasma to close the porosity. Study the response to the plasma technique to deposit suitable coating layers of silver on a medical Ti alloy to enhance its surface properties for biomedical applications. The surface of Ti 13Nb 13Zr alloy was engineered with a (TiO_2) by anodization and silver (Ag) by DC sputtering deposition; the tests are the optical microscope, scanning electron microscope, XRD, EDS, AFM, and contact angle; the results obtained in are presented and discussed to demonstrate the effect of surface modifications type each part of work will present and follow by the discussion of results. The results of XRD show two phases, TiO_2 and Ag; SEM results show coating thickness and the interface between TiO_2 and silver; EDS illustrated the weight percent of Ti, O, and Ag; AFM shows surface roughness of each coating layer, as contact angle showed the wettability of substrate or each layer surface and study corrosion behavior of each sample, while adhesion strength shows the efficiency of the coating layer.

1. Introduction

Titanium is the primary and extensively employed metallic implant material for challenging tissue applications [1-7]. Titanium and its alloys possess mechanical properties that facilitate their compatibility with bone. The low Young's modulus of titanium (Ti) mitigates stress shielding effects at the interface between the implant and bone [8]. Since titanium has excellent biocompatibility and outstanding mechanical qualities, it is currently the most extensively utilized material in producing biomaterial implants for treating bone fractures [9-13]. Dental implants, artificial cartilage for hip substitutes, artificial heart stents and valves, screws for bone and bone plates, and other medical devices are among the many different implantation applications that fall under the biomedical category [14]. Depending on the microstructure at room temperature, alloys made of titanium come

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in five varieties: α, near-α, α + β, metastable β, and stable β [15]. Anodic oxidation treatment is considered a more advantageous method due to its affordability, operational simplicity, and efficient coating process [16]. Consequently, titanium's surface can transform, enhancing its bioactivity [17]. β-titanium alloys containing Nb, Ta, and Zr as the main alloying elements at reduced Young's modulus values (≈60 GPa). Elements comprise a recently formed group of alloys for biomedical applications, which, compared to Ti-6Al-4V and CP Ti, is now more biocompatible and more akin to the mechanical characteristics of bones [18].

According to literature sources, β-titanium alloys have more strength and a lower modulus of elasticity in comparison to α or α + β Ti alloys. Because of this, a growing amount of focus has been submitted on creating a new generation of β Ti alloys that exclusively contain biocompatible elements in recent years [19-21]. Research indicates that alloys based on the Ti-Nb-Zr system may be more adaptive to environmental and medical circumstances in orthopedic applications than in dentistry applications [22].

There are two main factors contributing to the favorable properties of titanium implants: (1) the construction of a thick protective titanium oxide layer, which enhances corrosion resistance and biocompatibility, and (2) the formation of a rough and porous surface, which promotes effective osseointegration. The augmentation of surface roughness can elicit both advantageous and detrimental consequences at the interface between the tissue surrounding the implant and the implant itself. The advantage of this intervention will manifest as enhanced osseointegration between the bone and the implant. One aspect to consider is that micro topography has a significant role in establishing a robust and enduring connection between the surface of the implant and the surrounding peri-implant bone. This connection ultimately leads to the implant's secure and stable mechanical fixation [23].

In contrast, nanoscience can enhance bone cell adhesion by facilitating protein absorption and increasing the contact interface between proteins and cells. In addition, surface nanostructures were observed to promote the proliferation and development of osteoblasts and mesenchymal cells, thus facilitating the establishment of a suitable interface between the tissue surrounding the implant and the implant itself. However, the uneven texture of the surface has the potential to attract osteocytes that facilitate bone regeneration and bacteria that form a biofilm and cause inflammation at the implant site [24]. However, the trials indicated that silver nanoparticles impeded bacterial activity. Modifying roughness at the nano- and microscale levels impacts various physicochemical parameters, including the local surface electrostatic charge density and adhesion energy [25,26]. The surface is to be produced via physical surface modification techniques. These techniques include thermal spraying, ion implantation, physical vapor deposition, and glow discharge plasma treatments. Each approach produces a different layer of coating or film deposition on the surface of the titanium substrate; this is just the result of transmitting different types of energy. Therefore, an energy such as thermal, electrical, or kinetic force color is to be fabricated [27-29]. Gold, platinum, and gold-palladium alloys are frequently encountered as conductive metals. Sputtering can deposit a wide range of metallic materials onto textile substrates. One illustrative instance involves the extensive utilization of silver in functionalizing textiles. The anti-bacterial performance showed a positive correlation with the increase in film thickness. The prevailing belief was that augmenting the thickness of the coating unequivocally led to a heightened discharge of silver ions, enhancing the antimicrobial efficacy.

The user has provided a numerical reference, indicating the presence of a citation. In 2022, Jakubowicz [30] studied electrochemical anodic oxidation as a method for bio-functionalizing titanium surfaces. The investigation revealed that the titanium (Ti) surface is mainly coated with anatase-TiO_2 [31,32] following anodic oxidation in an electrolyte consisting of phosphoric acid

(H_3PO_4) and hydrofluoric acid (HF). The user provided a numerical reference without any accompanying text. Chopra *et al.,* [33] studied the surface modification of orthopedic implants made from titanium. In order to address diverse scenarios, the utilization of electrochemically anodized titanium (Ti) implants, including titania nanotubes (TNTs), has been proposed as a highly effective implant surface that possesses suitable bioactivity and the ability to release drugs locally. Raj *et al.,* [34] investigated the coating materials, TiN and Ag were coated on the bare and textured Ti-6Al-4V surfaces using DC magnetron sputtering in 2022. Emrah *et al.,* [35] investigated the effect of Ag^{+} coated conditions on the corrosion, tribo-corrosion, and anti-bacterial characteristics of Ti15Mo specimens in 2023.

In this research, we will rely on the formation of TiO_2 to Ti 13Nb 13Zr by anodizing and surface coating with a layer of metal (silver) using direct current sputtering technology to improve the surface properties. The silver coating was added. Conversely, by improving the absorption of protein and expanding the surface area that is in contact with both proteins and cells, nanotopography can encourage the attachment of bone cells. Moreover, surface nanostructures guarantee the appropriate implant-tissue contact and improve osteoblastic and mesenchymal cell growth and development. Nevertheless, the roughness of the surface would draw in bacteria that create a biofilm and inflame the implantation site in addition to the advantageous osteogenic cells.

2. Experimental Details

2.1 Materials and Methods

The Ti 13Nb13 Zr alloy was used as substrate specimens, 3mm in thickness and 13mm in diameter, and cut into cylinders by a wire cutting machine. The surface roughness was adjusted to Ra 0.08µm using SiC Abrasive papers (180-1000 grits) and washed completely with distilled water and dried hot air. Chemical analysis was conducted using an X-ray fluorescence (XRF) test available at the Ministry of Science and Technology in Baghdad, Iraq. Table 1 shows the chemical analysis of the Ti-13Nb-13Zr alloy (wt.%).

Table 1
Ti-13Nb-13Zr alloy (wt.%) chemical analysis

Elements	Zr	Nb	Fe	Mo	Zn	Mn	Cu	Ti	Residual element
Concentration (%)	15.22	13.45	0.11	0.07	0.05	0.03	0.04	Balance	0.13505

In order to reveal the grain boundaries in the microstructure, the specimens were treated with an etching solution known as Kroll's solution, which consists of 10 ml of hydrofluoric acid (HF), 5 ml of nitric acid (HNO_3), and 85 ml of water (H_2O) [36]. The pores have irregular but spherical shapes. The most common microstructure features in metallic materials are the interfaces between crystalline grains and the boundaries between different solid phases in multiphase alloys. Due to the direct influence of grain size and shape on material behavior, metallography offers a more straightforward comprehension of the connections between material microstructure and microscopic properties. The microstructure analysis indicates that the Ti-13Nb-13Zr alloy consists mostly of the α phase, with a small amount of the β phase present [37]. The material's structure is an alloy with a near-β configuration at normal ambient temperature, as seen in Figure 1.

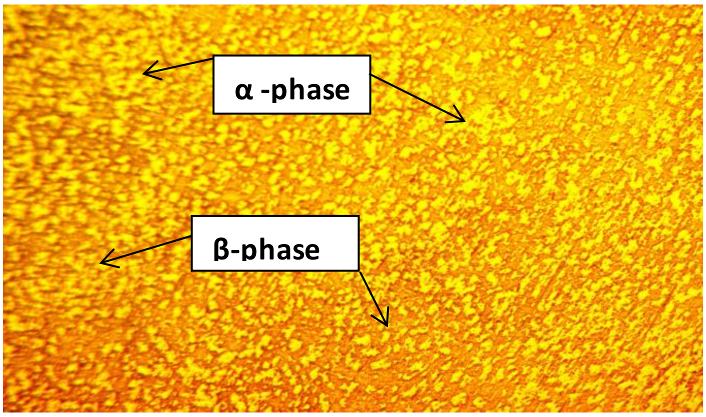


Fig. 1. Microstructure for Ti-13Nb-13Zr Alloy

2.2 Experimental Method
2.2.1 Anodizing process

The surface of Ti samples was modified utilizing an anodic oxidation method (0.8NaF,1MH_3PO_4) with two electrodes and stirring at room temperature. Ti alloy samples (13 thickness, 3 mm) and 316L alloy (13 thickness, 3 mm) were employed as anode and cathode. The prepared Ti sample and 316L stainless steel electrodes were carefully positioned in contact with the electrolyte in the cell. The electrode spacing distance was kept constant at 3 cm for all trials. Magnetic stirring was used to maintain homogenous particle dispersion during the anodic oxidation process in a beaker. The system was outfitted with a DC power supply with a potential (10 V) for 30 minutes. Following anodization, the specimens were rinsed in deionized water and air-dried.

2.2.2 DC sputtering deposition
2.2.2.1 Preparation of target coating

The target (Ag) metal has a diameter (of 48mm) and a thickness of (1.1 mm) and was manufactured by casting, which takes place in a gas furnace at a temperature of about 1000 Cº Then, a slag remover, which is borax, is added. The slag is then removed and poured into a flange-shaped cast iron mold 1 cm thick. Then, it was transferred to the rolling mill and rolled to the desired thickness (1.1 mm). After that, a circular disk with a diameter of (48 mm) was cut**.** The silver target, then cleaned and polished, was carried out for sputtering.

2.2.2.2 Coating process

The methodology of DC sputtering, a process conducted within a low-pressure gas device, was carried out using an argon discharge. The setup involved an evacuated chamber, a target (known as the cathode), and an anode made of Ti13Nb13Zr. The cathode was positioned opposite the gas discharge and subjected to a 4kV DC electrical field provided by a power supply. The anode was subsequently introduced. The bottommost portion of the cathode electrodes underwent modification using an insulator disk made of ceramic material. This assembly was enclosed within a quartz tube. The top electrodes had an observed diameter of 14.5 cm, whereas the target electrode, which represents the effective cathode dark space region, had a diameter of 7.5 cm. The vertical separation between the upper and target electrodes measured 4 centimeters. The gas source-flow controller system is responsible for delivering the specified rate of flow and pressure of gas of the feedstock to the plasma chamber. The system consists of dual-step controllers, fittings, and tubes that are exceptionally engineered for the containment and delivery of Argon. A two-stage needle valve controlled the plasma hollow's flow pressure.

An efficient vacuum system comprises a turbo pump (specifically, Variant, V-1000HT) supported by a hydraulic rotary pump (with a pumping capacity of $60m^3/h$, known as Blazer). In order to ensure proper monitoring of the pressure within the plasma chamber, it was necessary to establish a connection between the confinement system (Edward CP25-K, supervised by 1102) and the LH-Thermo vac. This connection facilitated the monitoring of both the actual pressure and the partial pressure of the discharge gases. Table 2 presents the DC spattering parameters.

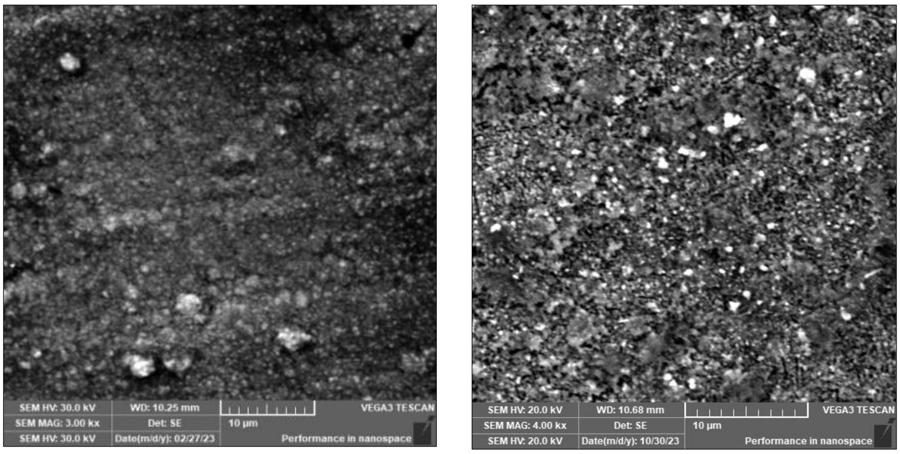
Table 2
Substrate the condition of Ti13Nb13Zr, which is coated by spattering using silver targets

Sputter chamber pressure (mbar)	Time (hour)	Voltage (V)	Current (mA)	Power (W)	Temp (°C)	Gas
6×10^{-2}	2	1400	20	30.8	200	Ar

3. Results and Discussion

3.1 Scanning Electron Microscope (SEM)

A scanning electron microscope (VEGA3SBU) was used to determine the morphology of the Ti alloy substrates. SEM and EDS imaging techniques examined the anodized specimens' shape and chemical composition. Figure 2 shows SEM pictures of the surface morphology of samples coated with (anodization and TiO_2/Ag multilayer coating).



(a) (b)

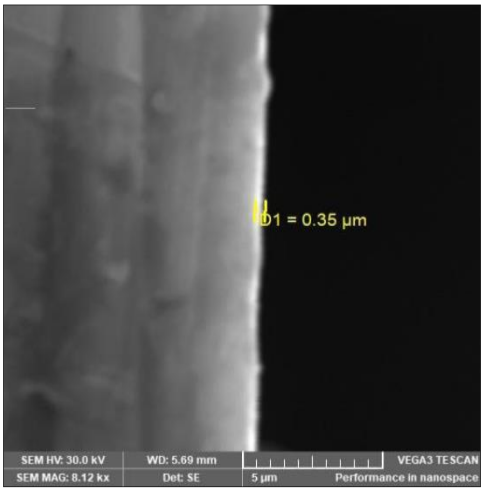
Fig. 2. SEM images (a) TiO_2 layer, (b) multilayer Coating

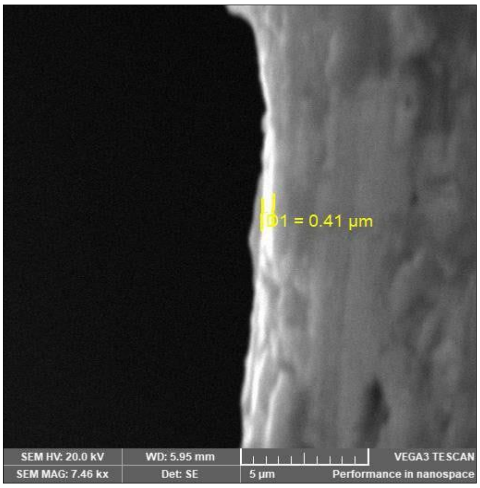
3.2 Thickness Measurements

Thickness values in Table 3 were estimated by lateral view SEM images. Figure 3 presents a cross-section view of the anodic oxide layer formed on the sample and silver coating. It is important to mention here that the increase in oxide film thickness can enhance bone formation [38]. Hence, in the present work, anodized oxide layers with thickness values of 350 nm were attained, which may be useful for osseointegration. The thickness of the deposited film was 148.27nm specimen after DC sputtering.

Table 3
The average thickness values of the coating formed over Ti 15Zr13Nb samples

Sample	Anodic TiO_2 layer	Multilayer (TiO_2/Ag) coating
Thickness (nm)	350	410





(a) (b)

Fig. 3. Cross-section SEM images (a) TiO_2 layer, (b) multilayer coating

3.3 X-Ray Diffraction Test Result (XRD)

The pattern of the base alloy in Figure 4 revealed the diffraction of the beta and alpha phases that matched the JCPDS Card No. (044 - 1294). It can be seen that the Ti15Zr13Nb alloy mainly consists of β -Ti and α –Ti [37], and the Ti-13Nb-13Zr alloy mainly consists of β -Ti and α –Ti.

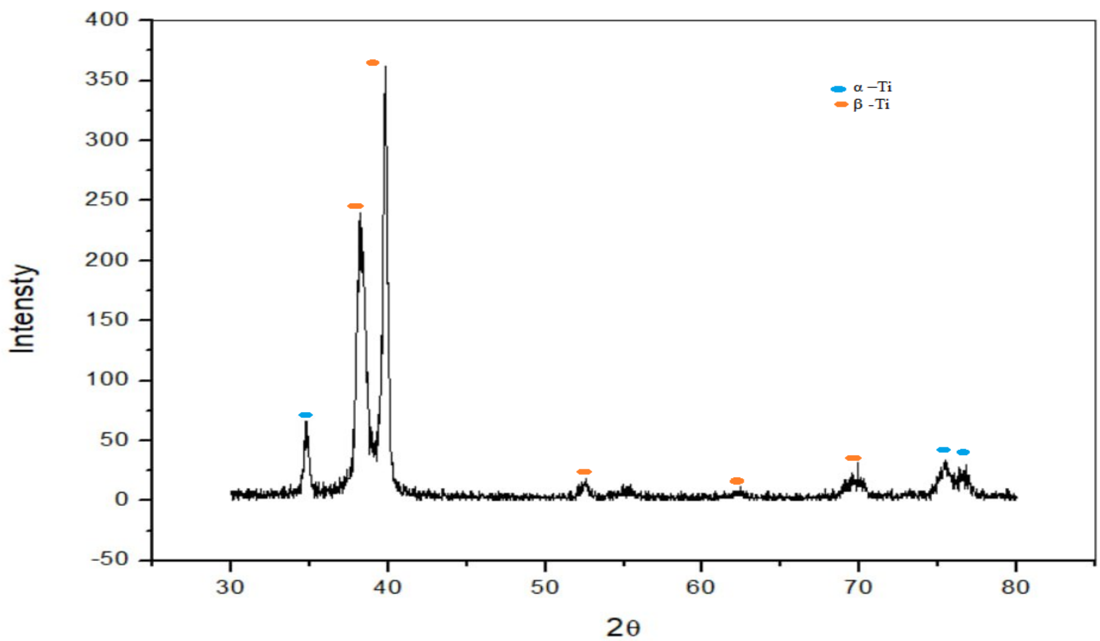


Fig. 4. XRD Pattern of Ti–13Nb–13Zr Alloy

Figure 5 shows the results of XRD analysis of the anodized surface under oxidation conditions (10V, 30min), corresponding to ICSD card number (017009). The XRD results confirm the formation of a TiO_2 layer with a similar crystalline phase in the treated Ti13Nb13Zr surface. The formed titanium dioxide–anatase-TiO2 (004), (112) and (105) direction.

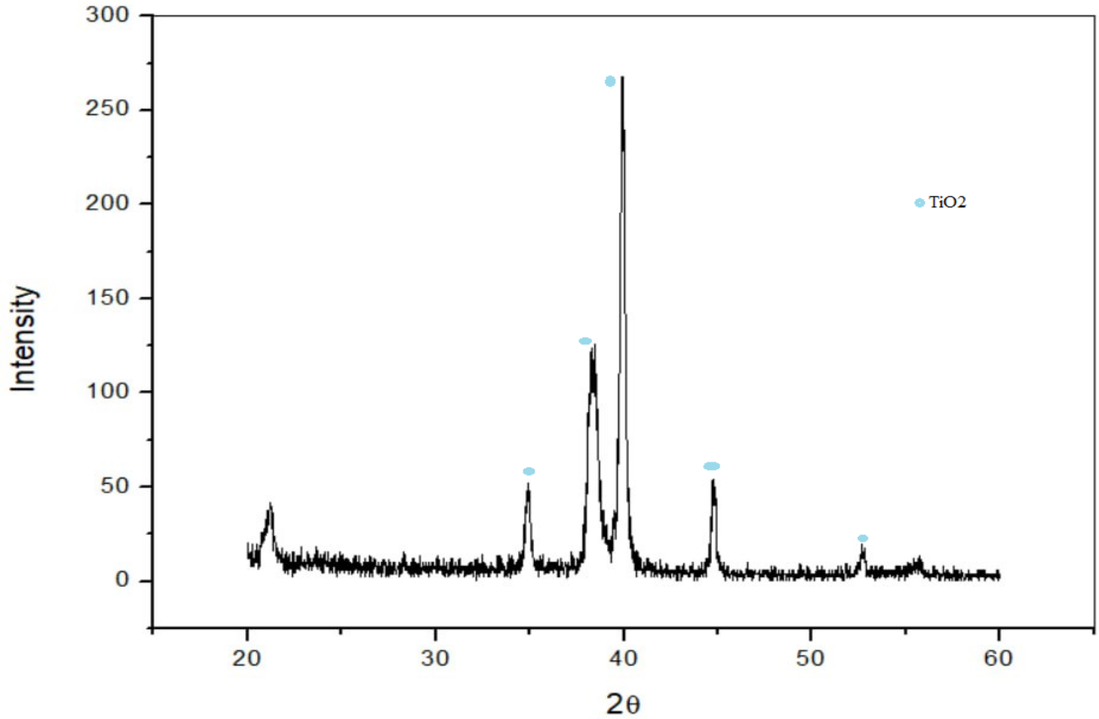


Fig. 5. XRD profiles of the anodized sample at (10 volts, 30min)

Figure 6 shows the XRD pattern of the as-sputtered Ag thin scale of the anodized sample (multilayer coating). From the d-spacing calculation, the diffraction rings can be indexed to be (111), (002), and (220) for Ag [39].

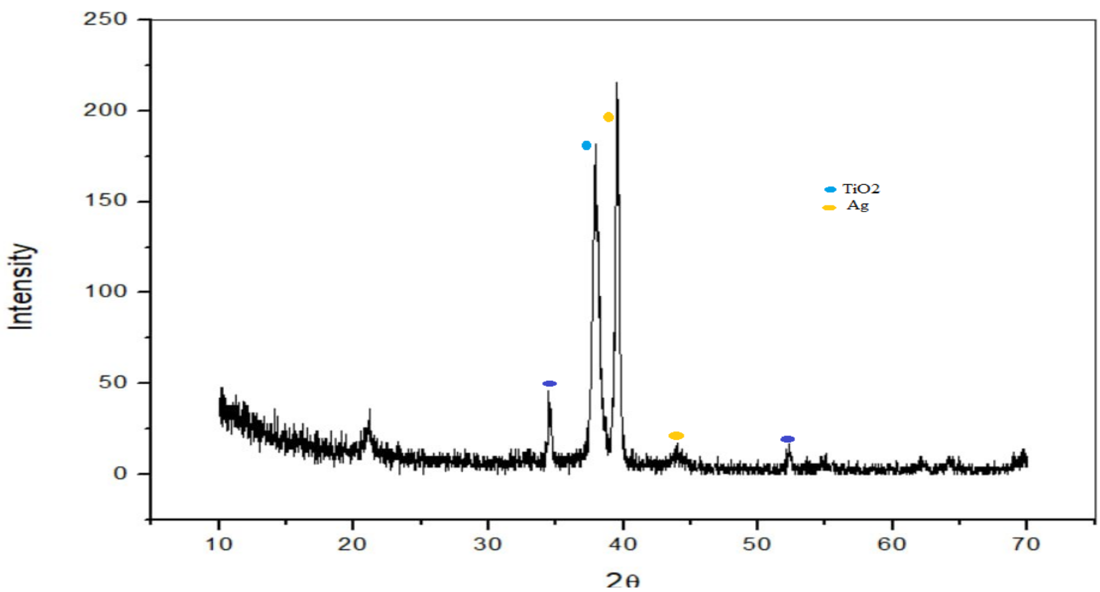


Fig. 6. XRD profiles of the multilayer coating

3.4 Energy Dispersive Spectroscopy (EDS)

Figure 7 shows the EDS analysis of Ti-13Nb13Zr surfaces modified after anodizing. The results confirm the formation of a Ti oxide layer in the sample due to higher amounts of Ti and O elements as the main components of TiO_2. Small amounts of N and Zr are also visible on the anodized surface.

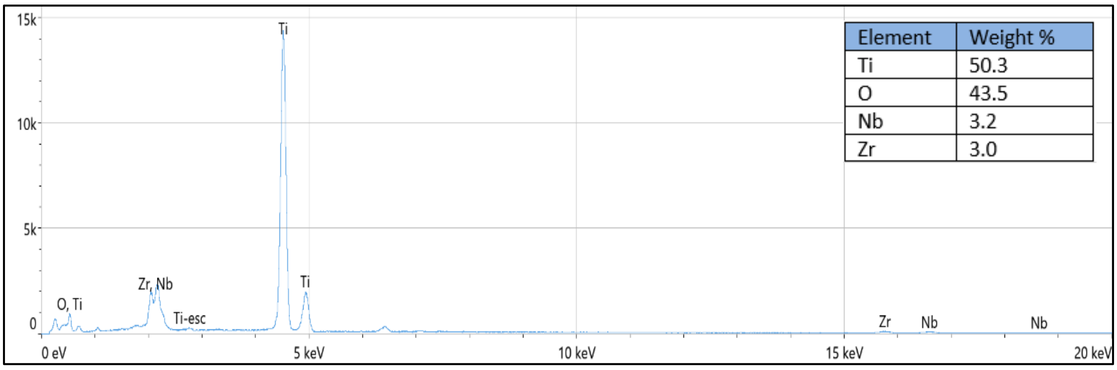


Fig. 7. EDS for TiO_2 layer

Figure 8 show the EDS analysis of Ti 13Nb 13Zr alloy modified with multilayer thin film formation (TiO_2) by oxidation and silver (Ag) by DC deposition. The elements in the treated sample were determined to be Ti, O, Ag, and a small amount of Nb, which matches the EDS analysis.

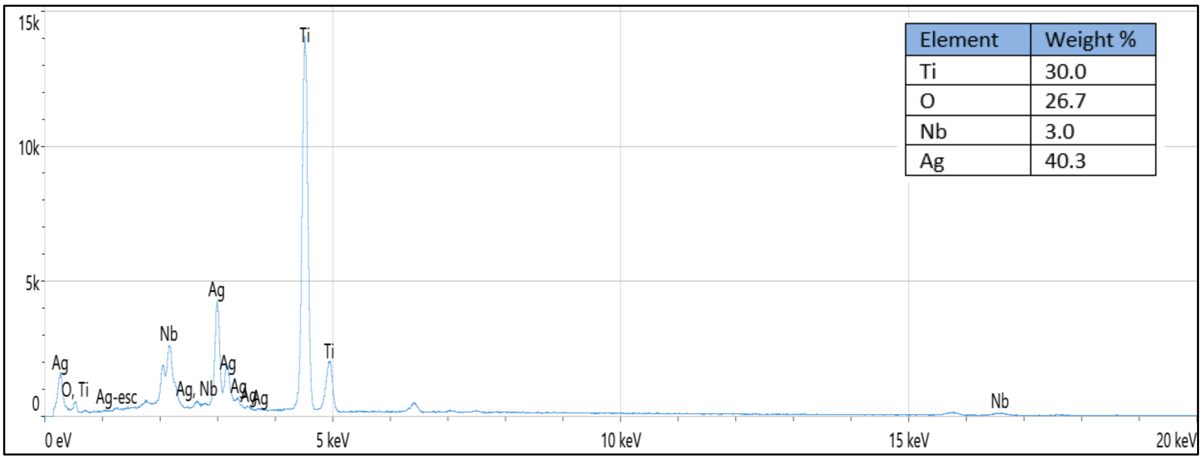


Fig. 8. EDS for multilayer (TiO_2/Ag)

3.5 Atomic Force Microscope (AFM)

AFM is a renowned technology used to map the topography and investigate the characteristics of materials at a nanoscale level. AFM observed the surface topography of investigated Ti 13Nb13Zr alloy samples, including 2D and 3D images and the partial size of the sample (AFM 2022, Nano surf, Switzerland).

Tables 4 and 5 show the results of an AFM test on Ti 13Nb13Zr alloy after anodizing and DC spraying. Compared to the DC spraying approach, the roughness values for the anodized sample were higher. The results accord well with the average roughness property obtained from the AFM test. Several studies have found that surface roughness in the (1 to 10) µm range increases interaction between the bone and the implant surface. When opposed to rougher surfaces, titanium with smoother surfaces has less interaction with bone [40], as shown in Figures 9 and 10.

Table 4
S q, S z, Sa AFM properties of TiO_2 layer

ISO- 25178-Primary Surface	
Sq (Root-mean-square height)	83.54 nm
Sz (Maximum height)	503.7 nm
Sa (Arithmetic mean height)	68.43 nm

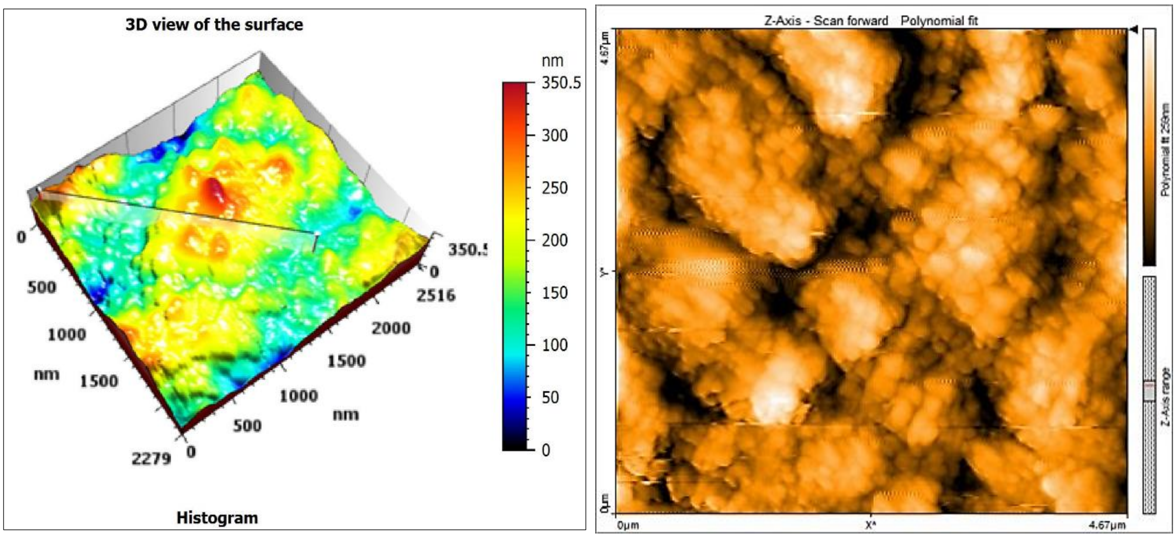


Fig. 9. AFM 2D, 3D profiles for anodization process at (10V,30min)

Table 5
S q, Sz and Sa AFM properties of multilayer coating

ISO- 25178-Primary Surface	
Sq (Root-mean-square height)	53.51nm
Sz (Maximum height)	337.6nm
Sa (Arithmetic mean height)	43.20nm

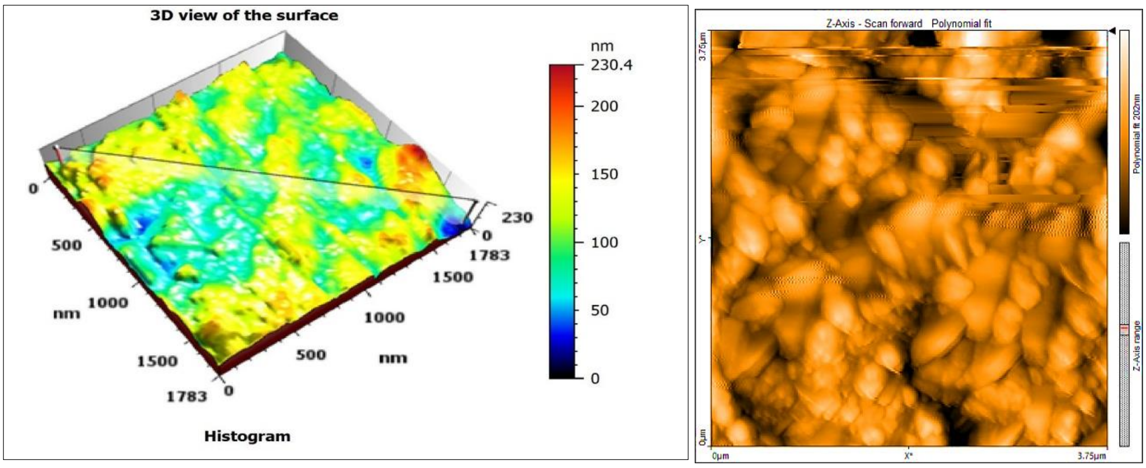


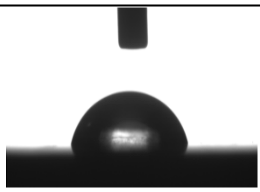
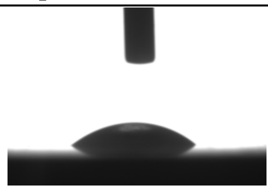
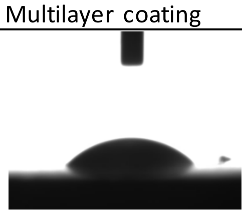
Fig. 10. AFM 2D, 3D profiles for multilayer coating

3.6 Contact Angle

The wettability of Ti-13Nb-13Zr alloy samples, both coated and uncoated, was assessed by measuring the contact angle (θ) of a droplet on the solid surface. The droplet employed was a typical salt solution (0.9% NaCl), and this measurement is a significant parameter for quantitatively evaluating wettability. The contact angle of water droplets on -Ti samples was measured using a CAM 11O-O4W optical contact angle device connected to a CCD camera. Table 4 displays the images captured before and after surface modification techniques, after application, and after 3-minute intervals. The contact angle of a titanium substrate was measured to be θ= 67.367º.

Similarly, the contact angles of samples subjected to anodization and silver coating were also determined. The experimental results indicated that the contact angles on the anodized samples were notably lower than those observed on the titanium alloy surface and the silver coating. This observation indicates that the wettability of the anodized titanium samples exhibited a notable increase compared to that of the original surface. The enhanced wettability of oxidized samples can be attributed to their increased overall Ra values compared to the bare substrate, as indicated by the roughness data presented in Tables 4 and 5. Numerous studies have demonstrated that augmenting the hydrophilic properties of the surface can yield a substantial enhancement in protein and cellular adhesion, in turn, can influence crucial biological processes such as cell proliferation and differentiation [41,42] and several other interactions between the implant surface and the surrounding biological milieu. Table 6 presents optical images depicting the contact angles observed on the substrate before and after anodizing and subsequent silver coating.

Table 6
Optical images of contact angles

Specimens	Base	TiO_2	Multilayer coating
Degree			
	67.367 º	30.203º	35.997 º

3.7 Adhesion Strength

Coating adherence to the implant surface is critical in medical applications, particularly long-term use. The ASTM-D4541 standard performed pull-off tests to assess the adhesion strength between the coating and the metal substrate. The adhesion strength of the coating layer after anodizing and silver coating was measured after 24h. The adhesion strength of TiO_2 (23.46). The highest adhesion resistance obtained was 26.12 MPa after multilayer.

For biomedical applications, it is essential to ensure that the layers have a minimal tensile strength of 18 MPa [43,44]; typically, this condition is disregarded when dealing with nanostructured surfaces. Narayanan *et al.,* [45,46] identified the adhesive strength of the nanotubes on titanium. The magnitude varied from 3.5 MPa to 13 MPa based on the conditions, and adhesion was enhanced by eliminating stress through swirling throughout nanotube production. In a study by Jia *et al.,* [47], the tensile bond strength of titanium nanotubes was assessed. The untreated nanotubes exhibited an adhesive strength of 1.4 MPa, while the polymer-treated nanotubes showed a higher adhesive strength of 4.4 MPa. According to Jaroslav Fojt *et al.,* [48], the researchers tested the adherence of the nanotubes utilizing an ASTM D 3359 tape test and a pull-off method (also known as a tensile test) with EPX DP 490 adhesive (Scotch-Weld). Tensile testing is recommended for calcium phosphate/substrate combinations or porous metal coating/substrate. This type of testing can provide valuable insights into the strength of coatings when subjected to tensile stress, whether adhesive or cohesive. A tensile load was placed on the coating/substrate contact at a crosshead speed of 1 mm/min until failure took place, at which point the measurement was carried out according to the ASTM standard. The adhesive strengths of the nanostructures manufactured at 20 V and 30 V were 38 3 MPa and 32 4 MPa, respectively. The adhesive strengths of these layers are more than sufficient for use on implants based on William *et al.,* [39]. A cellophane tape pull is used in the ASTM D3359 adhesion test. Three M610 cellophane tapes are utilized in the test. Pulling parallel to the substrate surface, the tape was removed. Following removal, the sample and tape were examined under an optical microscope for Ag fragments to assess adherence. Complete Ag film removal implies an adhesive failure (Ag film/substrate failure), whereas partial Ag film removal suggests a cohesive failure (failure inside the Ag film).

4. Conclusion

Two techniques for surface modification of titanium alloys for biomedical purposes. Anodizing process for (30) minutes at a voltage of (10) volts and distance of (3) cm. The second process is physical vapor deposition silver plating. Volatile plasma technology at a voltage of (1400 volts), a current of (20) mA, and a time of (2) hours. Tests were conducted for both methods. Getting multi-properties surface layers gathers high mechanical properties and biocompatibility. The results of SEM, XED and EDS revealed the formation of new phases in multilayer coating, which indicates that the surface modification conditions were perfect. In contrast, the results of AFM displayed a development in the roughness of the surface values of the surface-modified sample. As for the results of the adhesion resistance test, it was shown that the modified layer for all types of surface treatments used had an acceptable adhesion strength.

Reference

[1] Radhi, Nabaa S., Noor Emad Kareem, Zainab S. Al-Khafaji, Nebras Mohammed Sahi, and Mayadah W. Falah. "Investigation mechanical and biological properties of hybrid PMMA composite materials as prosthesis complete denture." *Egyptian Journal of Chemistry* 65, no. 10 (2022): 681-688.

[2] Al-Zubaidy, Basem, Nabaa S. Radhi, and Zainab S. Al-Khafaji. "Study the effect of thermal impact on the modelling of (titanium-titania) functionally graded materials by using finite element analysis." *International Journal of Mechanical Engineering and Technology* 1 (2019).

[3] Radhi, Nabaa S., and Z. A. I. N. A. B. Al-Khafaji. "Investigation biomedical corrosion of implant alloys in physiological environment." *Int J Mech Prod Eng Res Dev* 8, no. 4 (2018): 247-56. https://doi.org/10.24247/ijmperdaug201827

[4] Radhi, Nabaa S., Haydar H. Jamal Al-deen, Rasha Safaa Hadi, Nada Al-Ghaban, and Zainab S. Al-Khafaji. "Preparation And Investigation A Hydroxyapatite Layer Coating On Titanium Substrate For Surgical Implants." *Journal of Nanostructures* (2023).

[5] Abed Janabi, Zainab Makki, Haydar Shamkhi Jaber Alsalami, Zainab Sattar Al-Khafaji, and Safa A. Hussien. "Increasing of the corrosion resistance by preparing the trivalent nickel complex." *Egyptian Journal of Chemistry* 65, no. 6 (2022): 193-198.

[6] Lokman, Muhammad Quisar, Suraya Shaban, Suhaidi Shafie, Fauzan Ahmad, Hafizal Yahaya, Ahmad Mukifza Harun, and Mohd Azizi Abdul Rahman. "Improving Dye-Sensitized Solar Cells Photocurrent Performance based on Titanium Dioxide Photoanode Thickness." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 34, no. 1 (2024): 177-186. https://doi.org/10.37934/araset.34.1.177186

[7] John, Clera Peter, Roshafima Rasit Ali, Kamyar Shameli, Zatil Izzah Tarmizi, Mohd Shahrul Nizam Salleh, and Justin Chan Zhe. "Formulation of Titanium Dioxide Nanoparticles Using Sol-gel Technique." *Journal of Research in Nanoscience and Nanotechnology* 4, no. 1 (2021): 35-48.

[8] Niinomi, Mitsuo, and Masaaki Nakai. "Titanium-based biomaterials for preventing stress shielding between implant devices and bone." *International journal of biomaterials* 2011, no. 1 (2011): 836587. https://doi.org/10.1155/2011/836587

[9] Hussein, Eman Yasir, Jassim M. Salman Al-Murshdy, and Nabaa Sattar Radhi. "Functionally graded coating of titanium substrate in biomedical applications a review." In *AIP Conference Proceedings*, vol. 2977, no. 1. AIP Publishing, 2023. https://doi.org/10.1063/5.0183555

[10] Jasim, Ahlam H., Wafaa M. Joudi, Nabaa S. Radhi, and Amir N. Saud. "Mechanical properties and wear characteristic of (Aluminum-Zinc Oxide) metal matrix composite prepared using stir casting process." In *Materials science forum*,

vol. 1002, pp. 175-184. Trans Tech Publications Ltd, 2020. https://doi.org/10.4028/www.scientific.net/MSF.1002.175

[11] Jasim, Ahlam Hamid, Nabaa S. Radhi, Noor Emad Kareem, Zainab S. Al-Khafaji, and Mayadah Falah. "Identification and investigation of corrosion behavior of electroless composite coating on steel substrate." *Open Engineering* 13, no. 1 (2023): 20220472. https://doi.org/10.1515/eng-2022-0472

[12] N. S. Radhi, A. H. Jasim, Z. S. Al-Khafaji, and M. Falah, *Investigation of Hematite Nanoparticles According to Mechanical Characteristics of Aluminium Matrix Composite.*, Nanosistemi, Nanomateriali, Nanotehnologii, (2023).

[13] K. M. Abed, N. S. Radhi, A. H. Jasim, Z. S. Al-Khafaji, S. Radhi, and S. A. Hussien, *Study the effect of adding zirconia particles to nickel–phosphorus electroless coatings as product innovation on stainless steel substrate*, Open Engineering, (2022). https://doi.org/10.1515/eng-2022-0364

[14] S. A. Salihu, Y. I. Suleiman, and A. I. Eyinavi, *Classification, Properties and Applications of titanium and its alloys used in automotive industry—A Review*, Am. J. Eng. Res, (2019).

[15] F. D. Al-Shalawi *et al.*, *Biomaterials as implants in the orthopedic field for regenerative medicine: metal versus synthetic polymers*, Polymers, (2023). https://doi.org/10.3390/polym15122601

[16] S. A. Hamza and N. S. Radhi, *Composite Coating Using (Hap-Nano Silver) By Macro Arc Oxidation Procedures Was Used To Study the in-Vivo Properties of Titanium Substrate*, Academic Journal of Manufacturing Engineering, (2023).

[17] Z. S. Al-khafaji, N. S. Radhi, and S. A. Mohson, *Preparation and modelling of composite materials (polyester-alumina) as implant in human body*, International Journal of Mechanical Engineering and Technology, (2018).

[18] M. Niinomi, Y. Liu, M. Nakai, H. Liu, and H. Li, *Biomedical titanium alloys with Young's moduli close to that of cortical bone*, Regenerative biomaterials, (2016). https://doi.org/10.1093/rb/rbw016

[19] S. G. Schneider, C. A. Nunes, S. O. Rogero, O. Z. Higa, and J. C. Bressiani, *Mechanical properties and cytotoxic evaluation of the Ti-3Nb-13Zr alloy*, Biomecánica, (2000). https://doi.org/10.5821/sibb.v8i1.1653

[20] V. Hoppe, P. Szymczyk-Ziółkowska, M. Rusińska, B. Dybała, D. Poradowski, and M. Janeczek, *Assessment of mechanical, chemical, and biological properties of Ti-Nb-Zr alloy for medical applications*, Materials, (2020). https://doi.org/10.3390/ma14010126

[21] Jasim Ahmed Jasim;, A. Yaser, and Z. Al-Khafaji, *AN ANSYS SIMULATION STUDY ON THE EFFECT OF APPLYING TITANIUM ALLOY (TI-6AL-4V) COATING FOR WIND TURBINE GEAR*, Academic Journal of Manufacturing Engineering, (2024).

[22] Dinu, M., S. Franchi, V. Pruna, C. M. Cotrut, V. Secchi, M. Santi, I. Titorencu, C. Battocchio, G. Iucci, and A. Vladescu. "Ti-Nb-Zr system and its surface biofunctionalization for biomedical applications." In *Titanium in Medical and Dental Applications*, pp. 175-200. Woodhead Publishing, 2018. https://doi.org/10.1016/B978-0-12-812456-7.00008-1

[23] Branemark, Per-Ingvar. "Osseointegrated implants in the treatment of the edentulous jaw: experience from a 10-year period." *Scad J Plast Reconstr Surg* 16 (1977): 1-132.

[24] Huo, Kaifu, Xuming Zhang, Hairong Wang, Lingzhou Zhao, Xuanyong Liu, and Paul K. Chu. "Osteogenic activity and antibacterial effects on titanium surfaces modified with Zn-incorporated nanotube arrays." *Biomaterials* 34, no. 13 (2013): 3467-3478. https://doi.org/10.1016/j.biomaterials.2013.01.071

[25] Gongadze, Ekaterina, Doron Kabaso, Sebastian Bauer, Tomaž Slivnik, Patrik Schmuki, Ursula van Rienen, and Aleš Iglič. "Adhesion of osteoblasts to a nanorough titanium implant surface." *International journal of nanomedicine* (2011): 1801-1816. https://doi.org/10.2147/IJN.S21755

[26] Fahad, Nesreen Dakhel, Nabaa Sattar Radhi, Zainab S. Al-Khafaji, and Abass Ali Diwan. "Surface modification of hybrid composite multilayers spin cold spraying for biomedical duplex stainless steel." *Heliyon* 9, no. 3 (2023). https://doi.org/10.1016/j.heliyon.2023.e14103

[27] Sarraf, M., E. Zalnezhad, A. R. Bushroa, A. M. S. Hamouda, A. R. Rafieerad, and B. Nasiri-Tabrizi. "Effect of microstructural evolution on wettability and tribological behavior of TiO2 nanotubular arrays coated on Ti–6Al–4V." *Ceramics International* 41, no. 6 (2015): 7952-7962. https://doi.org/10.1016/j.ceramint.2015.02.136

[28] Praharaj, Rinmayee, Snigdha Mishra, and Tapash R. Rautray. "The structural and bioactive behaviour of strontium-doped titanium dioxide nanorods." *Journal of the Korean Ceramic Society* 57, no. 3 (2020): 271-280. https://doi.org/10.1007/s43207-020-00027-y

[29] Zalnezhad, Erfan, Elaheh Maleki, Seyedeh M. Banihashemian, Joon W. Park, Young-Beom Kim, Masoud Sarraf, Ahmed Aly Diaa Mohammed Sarhan, and Singh Ramesh. "Wettability, structural and optical properties investigation of TiO2 nanotubular arrays." *Materials Research Bulletin* 78 (2016): 179-185. https://doi.org/10.1016/j.materresbull.2016.01.035

[30] Jakubowicz, J., G. Adamek, and L. Smardz. "Porous surface state analysis of anodized titanium for biomedical applications." *Metallurgical and Materials Transactions A* 53 (2022): 86-94. https://doi.org/10.1007/s11661-021-06492-2

[31] Abdelhamed, Abdelrahman Hamed Ebrahem, Kah-Yoong Chan, Benedict Wen-Cheun Au, Gregory Soon How Thien,

Pei-Ling Low, Yew-Keong Sin, Chu-Liang Lee, and Wai-Leong Pang. "Electrochromic Properties of Sol-Gel Deposited Electrochromic TiO2 Thin Films." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 31, no. 2 (2023): 71-80. https://doi.org/10.37934/araset.31.2.7180
[32] Anuar, Shairazi Akmal, Mohd Fauzi Ab Rahman, Amal Muaz Nasir, Anas Abdul Latiff, and Afiq Arif Aminuddin Jafry. "Q-switched erbium-doped fiber laser generation using titanium aluminum carbonitride Ti3Al (C0. 5N0. 5) 2 saturable absorber." *Journal of Advanced Research in Applied Sciences and Engineering Technology* 31, no. 1 (2023): 144-155. https://doi.org/10.37934/araset.31.1.144155
[33] Chopra, Divya, Karan Gulati, and Sašo Ivanovski. "Understanding and optimizing the antibacterial functions of anodized nano-engineered titanium implants." *Acta Biomaterialia* 127 (2021): 80-101. https://doi.org/10.1016/j.actbio.2021.03.027
[34] Raj, Akash, Priyanka CP, and Ramachandrann KK. "Characterization of Ti biomedical implant surfaces modified by physical vapour deposition coating." In *Proceedings of the International Conference on Aerospace & Mechanical Engineering (ICAME 21)*. 2022. https://doi.org/10.2139/ssrn.4042645
[35] Meletlioglu, Emrah, and Recep Sadeler. "Comparison of corrosion, tribocorrosion and antibacterial properties of silver coatings on Ti15Mo by magnetron sputtering." *Surface Review and Letters* 30, no. 05 (2023): 2350027. https://doi.org/10.1142/S0218625X23500270
[36] Dai, Nianwei, Lai-Chang Zhang, Junxi Zhang, Qimeng Chen, and Maoliang Wu. "Corrosion behavior of selective laser melted Ti-6Al-4 V alloy in NaCl solution." *Corrosion Science* 102 (2016): 484-489. https://doi.org/10.1016/j.corsci.2015.10.041
[37] Ossowska, Agnieszka, Andrzej Zieliński, Jean-Marc Olive, Andrzej Wojtowicz, and Piotr Szweda. "Influence of Two-Stage Anodization on Properties of the Oxide Coatings on the Ti–13Nb–13Zr Alloy." *Coatings* 10, no. 8 (2020): 707. https://doi.org/10.3390/coatings10080707
[38] Larsson, Cc, P. Thomsen, J. Lausmaa, M. Rodahl, B. Kasemo, and L. E. Ericson. "Bone response to surface modified titanium implants: studies on electropolished implants with different oxide thicknesses and morphology." *Biomaterials* 15, no. 13 (1994): 1062-1074. https://doi.org/10.1016/0142-9612(94)90092-2
[39] Fordham, William R., Sean Redmond, Adam Westerland, E. G. Cortes, C. Walker, C. Gallagher, C. J. Medina et al. "Silver as a bactericidal coating for biomedical implants." *Surface and Coatings Technology* 253 (2014): 52-57. https://doi.org/10.1016/j.surfcoat.2014.05.013
[40] Likibi, F., M. Assad, C. Coillard, G. Chabot, and C. H. Rivard. "Bone integration and apposition of porous and non porous metallic orthopaedic biomaterials." In *Annales de chirurgie*, vol. 130, no. 4, pp. 235-241. 2005. https://doi.org/10.1016/j.anchir.2004.12.006
[41] Minagar, Sepideh, Yuncang Li, Christopher C. Berndt, and Cuie Wen. "Cell response and bioactivity of titania–zirconia–zirconium titanate nanotubes with different nanoscale topographies fabricated in a non-aqueous electrolyte." *Biomaterials science* 3, no. 4 (2015): 636-644. https://doi.org/10.1039/C5BM00007F
[42] Wang, Yu, Cuie Wen, Peter Hodgson, and Yuncang Li. "Biocompatibility of TiO2 nanotubes with different topographies." *Journal of Biomedical Materials Research Part A* 102, no. 3 (2014): 743-751. https://doi.org/10.1002/jbm.a.34738
[43] Kar, A., K. S. Raja, and M. Misra. "Electrodeposition of hydroxyapatite onto nanotubular TiO2 for implant applications." *Surface and Coatings Technology* 201, no. 6 (2006): 3723-3731. https://doi.org/10.1016/j.surfcoat.2006.09.008
[44] Dawood, Nawal Mohammed, Nabaa S. Radhi, and Zainab S. Al-Khafaji. "Investigation corrosion and wear behavior of Nickel-Nano silicon carbide on stainless steel 316L." In *Materials Science Forum*, vol. 1002, pp. 33-43. Trans Tech Publications Ltd, 2020. https://doi.org/10.4028/www.scientific.net/MSF.1002.33
[45] Narayanan, R., Tae-Yub Kwon, and Kyo-Han Kim. "TiO2 nanotubes from stirred glycerol/NH4F electrolyte: roughness, wetting behavior and adhesion for implant applications." *Materials Chemistry and Physics* 117, no. 2-3 (2009): 460-464. https://doi.org/10.1016/j.matchemphys.2009.06.023
[46] Narayanan, R., Jung-Yun Ha, Tae-Yub Kwon, and Kyo-Han Kim. "Structure and properties of self-organized TiO 2 nanotubes from stirred baths." *Metallurgical and Materials Transactions B* 39 (2008): 493-499. https://doi.org/10.1007/s11663-008-9153-7
[47] Jia, Huiying, and Lei L. Kerr. "Sustained ibuprofen release using composite poly (lactic-co-glycolic acid)/titanium dioxide nanotubes from Ti implant surface." *Journal of pharmaceutical sciences* 102, no. 7 (2013): 2341-2348. https://doi.org/10.1002/jps.23580
[48] Fojt, Jaroslav, Vladimir Filip, and Ludek Joska. "On the increasing of adhesive strength of nanotube layers on beta titanium alloys for medical applications." *Applied Surface Science* 355 (2015): 52-58. https://doi.org/10.1016/j.apsusc.2015.07.074