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Study on the Preparation and Properties of Biologically Functional Micro-arc Oxidation Coatings Containing Phosphorus on Titanium Alloys

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Abstract

In this study, a biologically functional micro-arc oxidation film was prepared on the surface of TA2. An oxidized ceramic layer was formed on the surface of the material by applying different micro-arc oxidation voltages in the MAO electrolyte. The applied voltage has a significant impact on the relevant characteristics after micro-arc oxidation. As the voltage increases, the pore size and the thickness of the film layer continuously increase. When the voltage exceeds 400V, the oxygen content decreases, and the porosity also decreases accordingly. With the increase of the voltage, the diffraction peaks of the rutile phase with thermal stability in the coating gradually increase due to the rise of the surface energy density of the sample. When the voltage reaches 400V, it has a relatively high porosity, hydrophilicity, and corrosion resistance, which gradually decrease as the voltage continues to increase to 500V.

Keywords

Hydrophilicity; Microarc Oxidation; Oxidation Voltage; Roughness; Corrosion.

1. Introduction

Titanium, a metallic element with significant applications in various fields such as aerospace and chemical engineering, has an abundance of approximately 0.63% in the Earth's crust. It is one of the relatively abundant elements in the Earth's crust, second only to common metals like iron, aluminum, and magnesium. Despite its unique advantages and broad application prospects, titanium has some limitations that cannot be ignored in practical applicationss[1,2].

Firstly, titanium has relatively active chemical properties and is highly prone to reacting with elements such as oxygen, nitrogen, and hydrogen in high-temperature environments. This makes the smelting process of titanium complex and costly. In nature, titanium mainly exists in the form of minerals such as ilmenite ($FeTiO_3$) and rutile (TiO_2). Secondly, the strength of pure titanium is relatively limited, with its tensile strength generally ranging from 240-340 MPa. In some heavy-duty industrial application scenarios with extremely high strength requirements, pure titanium is difficult to independently serve as a structural material.

To overcome these problems, researchers in the field of materials science have adopted various methods to modify titanium. Among them, alloying technology is one of the most commonly used methods[3]. By adding other elements (such as aluminum, vanadium, molybdenum, etc.) to titanium, a series of titanium alloy materials with excellent properties have been successfully developed. The mechanical properties such as strength and toughness of these titanium alloys have been significantly improved compared with pure titanium. For example, the tensile strength of the Ti-6Al-4V alloy can reach more than 900 MPa.

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In the current clinical application fields of orthopedics and dentistry, compared with stainless steel and nickel-based alloys, titanium and its alloys are gradually taking the dominant position. This is mainly attributed to their multiple outstanding properties: a higher specific strength, which means they can bear a greater load under the same weight; a lower elastic modulus, which makes their mechanical properties more compatible with human bones and can effectively reduce the stress shielding effect; excellent biocompatibility, which can reduce the rejection reaction of the human immune system; and excellent corrosion resistance, which can ensure long-term stable existence in the complex physiological environment of the human body[4].

However, titanium and its alloys still have a certain degree of biological inertness in clinical applications. When implanted into the human body, it may trigger the phenomenon of fibrous encapsulation. This is like forming a barrier between the implant and the bone tissue, hindering the direct contact between the two[5]. This not only affects the integration effect of the implant and the bone tissue but also increases the potential risk of the implant losing stability during long-term use, which may lead to the failure of the implantation surgery in the later stage.

To solve this problem, researchers and clinicians generally use surface treatment technology to modify the surface of titanium alloys. In this way, the surface of titanium alloys can be endowed with biological activity, promoting their close combination with bone tissue and improving the long-term stability of the implant, thus further expanding the application prospects of titanium and its alloys in orthopedic and dental clinical treatments[6].

Due to their good corrosion resistance, mechanical properties, excellent stability, and biocompatibility, titanium and its alloys have become excellent choices for alternative materials for repairing human bone tissues. They are widely used in the field of bone implantation, such as joint prostheses and dental implants[7]. Their Young's modulus is similar to that of human bones. However, they have biological inertness, resulting in poor osseointegration ability and difficulty in effectively combining with the surrounding bone tissue, which affects the success rate of the surgery. Moreover, they lack antibacterial properties, and the implants are prone to bacterial infections, posing a threat to the lives of diabetic patients. Although preparing biofunctional coatings on their surfaces through micro-arc oxidation can enhance the osseointegration ability, and subsequent hydrothermal treatment can further enhance the biological activity, in order to overcome the above disadvantages, developing a dual-functional coating with good antibacterial and osteoinductive activities is still crucial for promoting the development of titanium implants.

Micro-arc oxidation (MAO) is a surface treatment technology that improves the properties of materials by forming a micro-porous oxide layer on the metal surface.This technology is usually applicable to metal materials such as aluminum alloys and titanium alloys[8]. The process of micro-arc oxidation is to use a DC power supply or an AC power supply to conduct electrolytic treatment on the surface of the workpiece in an electrolyte solution[9]. Under high pressure, a rough, porous, dense, uniform, high-hardness, wear-resistant, and corrosion-resistant ceramic oxide film is in-situ grown on the surface of the substrate[10]. Through the micro-arc oxidation technology, the osseointegration performance of titanium with human tissues can be greatly improved, and thus its biocompatibility can be enhanced. After it was first discovered by Gunterschultze and Betz in the 20th century, it has now become a key research direction for scholars at home and abroad.

The research focus of this paper is to prepare a bioactive micro-arc oxidation coating containing phosphorus on titanium alloys and improve its hydrophilicity, corrosion resistance, and antibacterial properties[11]. By adjusting the oxidation voltage and time, suitable micro-arc oxidation parameters for the material can be found, thereby improving the long-term stability and implantation success rate of the implant.

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2. Material and Methods

2.1 Experimental Materials and Pretreatment

In this paper, during the synthesis of the micro-arc oxidation film, in order to ensure the smooth progress of the micro-arc oxidation process of the film, the pure titanium (TA2) needs to be cut and cleaned according to specific dimensions. The specific operations are as follows: Use a wire electrical discharge machine to cut the pure titanium (TA2) into thin slices with a diameter of Φ14mm and a thickness of 1.5mm. And at a position 1mm away from the edge of the thin slice, a hole with a diameter of Φ3mm is drilled. This hole is used to fix the fixture during the micro-arc oxidation process, and its position and size can refer to Figure 3.2. After the cutting is completed, use SiC sandpapers with grit numbers of 200#, 400#, 800#, 1000#, 1500#, and 2000# to grind the titanium slices step by step. Ultrasonic cleaning: Put the ground titanium slices into deionized water and absolute ethanol successively, and perform ultrasonic washing for 5 minutes each time, which can effectively remove the oil stains remaining during the cutting process and achieve the purpose of degreasing. After the cleaning is completed, place the titanium slices in a drying oven for storage to prevent them from being oxidized or contaminated with impurities before subsequent use.

2.2 Selection of Electrical Parameters and Electrolyte Configuration

In this experiment, the MAO30HD-III micro-arc oxidation power supply system is adopted, which has the characteristics of flexible parameter adjustment and intelligent operation. The power supply mode is the constant voltage mode, and the selected voltages are 300 V, 350 V, 400 V, 450 V, and 500 V. Micro-arc oxidation is carried out in an electrolyte solution consisting of 10 g/L $(NaPO_3)x$, 10 g/L $Na_3PO_4 \cdot 12H_2O$, 5 g/L KOH, and 5 ml/L $C_3H_8O_3$. The selected mode is constant voltage, the frequency is 500 Hz, the duty cycle is 5%, and the reaction temperature ranges between 15 °C and 25 °C.

2.3 Characterization of MAO Coating

The hydrophilicity of the coating surface was measured using a K100-MK2 interfacial tension measuring instrument.AQUANTA FEG 450 field emission ambient SEM was utilized to observe the surface and cross-section topography of the MAO films. A D8 ADVANCE model XRD was used to characterise the surface phases of the MAO films. The coating corrosion endurance measurements were conducted using an electrochemical workstation, model CHI760E, manufactured by Shanghai Chenhua Co. Ltd.

3. Results and Discussion

3.1 Surface Morphology of MAO Coatings

Figure1 shows the SEM images of the microscopic morphology of the MAO (Micro-Arc Oxidation) film layers on titanium sheets formed under different voltages. The surface of the titanium sheets treated by micro-arc oxidation exhibits the microscopic structural characteristics of a rough and porous "crater" shape. The formation mechanism of this special morphology can be attributed to the local high temperature generated on the substrate surface due to the discharge effect, which causes the molten titanium oxide substances to be ejected to the outermost surface through these "discharge channels". When in contact with the low-temperature electrolyte, a rapid cooling effect occurs, and the molten titanium oxide rapidly solidifies and accumulates at the openings of the "discharge channels".

Different voltages have a significant impact on the morphological changes of the oxide film layers. With the increase of the voltage during the micro-arc oxidation process, the substances inside the film layer will flow under the influence of factors such as high temperature and the electric field. In the early stage, due to the uneven growth of the film layer and the differences in local reactions, the flow direction of the substances in the micro-pores is relatively chaotic, resulting in irregular shapes of the micro-pores. As the reaction proceeds, the substance flow will be affected by the surface tension.

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When the molten substances in the film layer flow around the micro-pores, the surface tension will prompt the substances to transform into a state with the lowest energy. Under the equilibrium effect of the surface tension, the shape gradually changes into a circular shape. The shape of the micro-pores on the surface of the oxide film layer also changes from small pores and various irregular elongated shapes to circular shapes, and the diameter becomes larger. When the voltage increases to between 450 V and 500 V, some of the holes are melted and closed, and some show the shape of a crater eruption. The number of holes decreases, and the porosity becomes smaller.The results show that MAO-400 V has a suitable micro-pore size and a dense and uniform oxide layer.

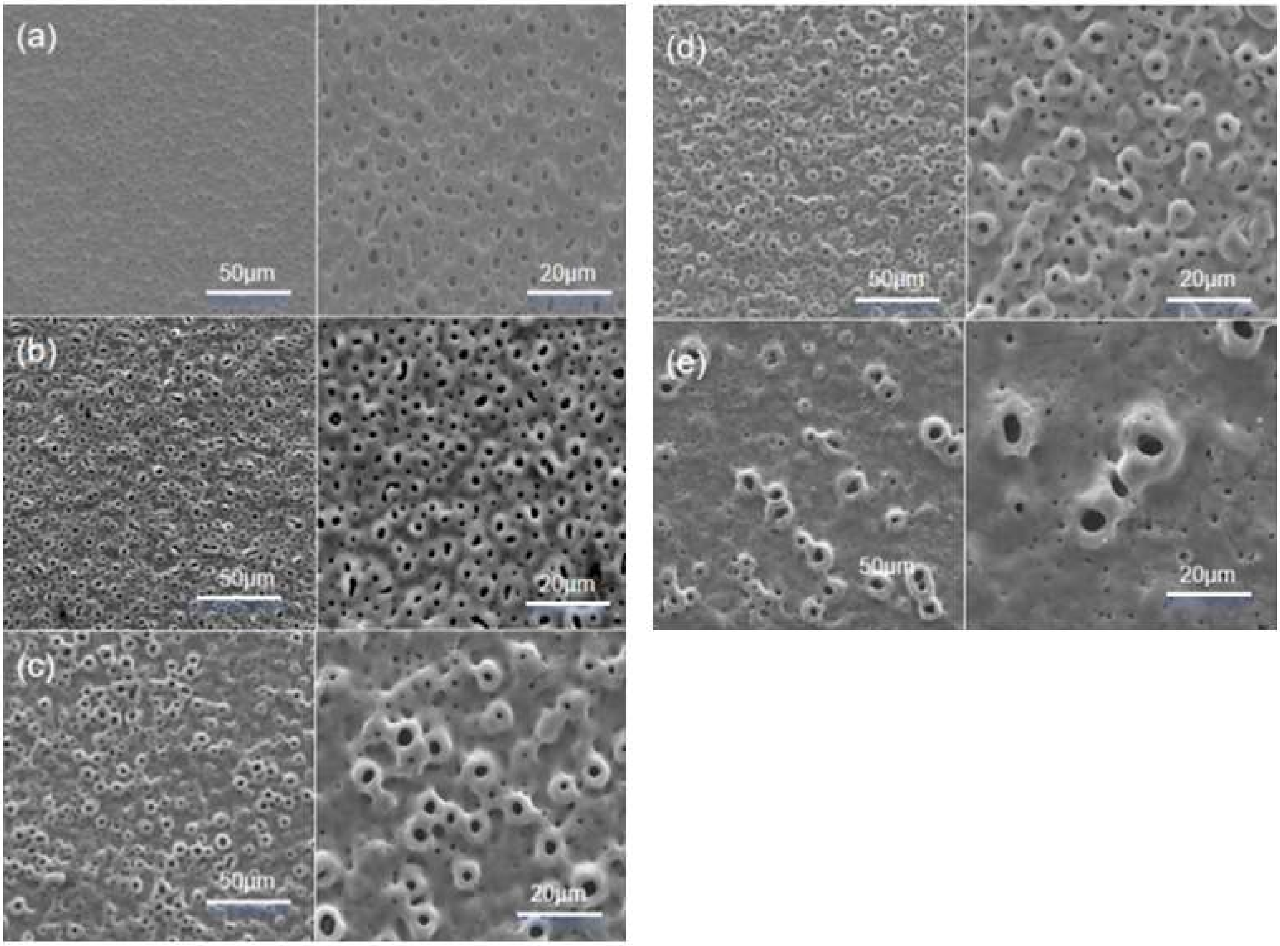

Figure 1. Micromorphology of oxide layer under different oxidation voltages: (a) 300 V; (b) 350 V; (c) 400 V; (d) 450 V; (e) 500 V

As shown in Figure 2, the professional software Image J was used to perform binary processing and analysis on the SEM images of the sample surfaces at a magnification of 2000 under different voltages in Figure 3.3. The porosities of MAO-300 V, MAO-350 V, MAO-400 V, MAO-450 V, and MAO-500 V were obtained as 3.81%, 5.47%, 9.26%, 7.57%, and 4.34%, respectively. The porosities of all the film layers, from largest to smallest, are as follows: 400 V > 450 V > 350 V > 300 V > 500 V. With the increase of the applied voltage, the porosity of the film layer shows a trend of first increasing and then decreasing. As the applied voltage gradually increases during the micro-arc oxidation (MAO) treatment process, the size of the micro-pores on the surface of the film layer exhibits a significant increasing trend.

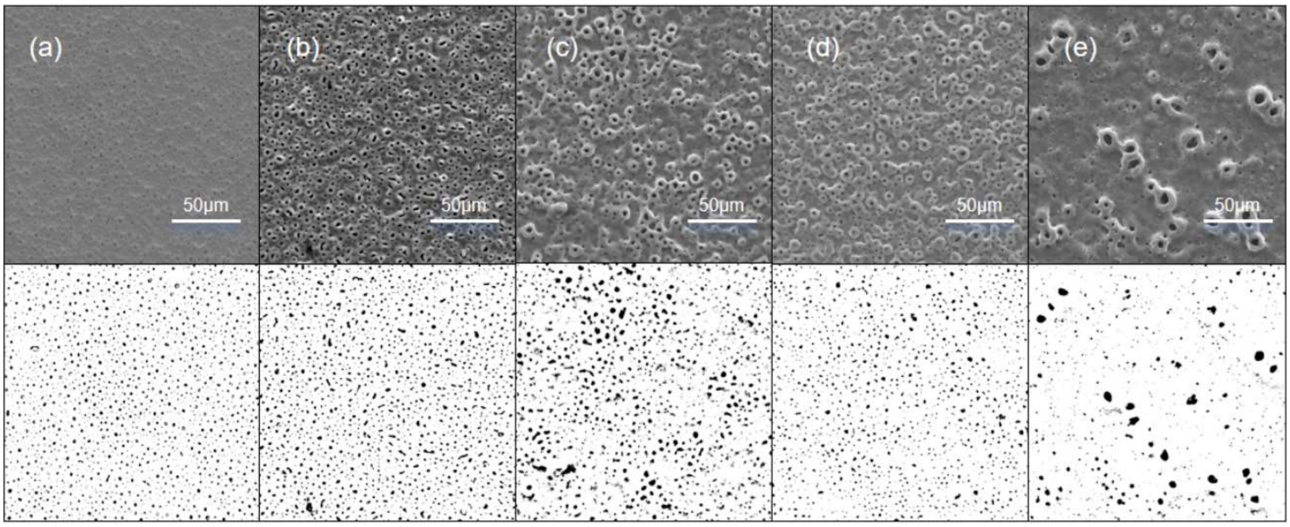

Figure 2. Binary images corresponding to the SEM images of the sample film layers at (a) 300 V; (b) 350 V; (c) 400 V; (d) 450 V; (e) 500 V

3.2 Phase Composition Analysis of Oxide Layer

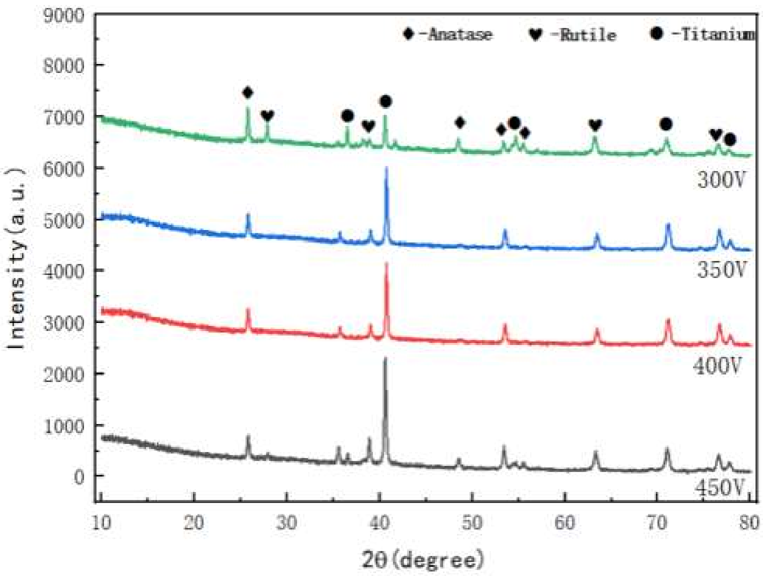

Figure 3. XRD patterns of oxide layers at different oxidation voltages (a) 300V, (b) 350V, (c) 400V, (d) 450V

As can be seen from Figure 3, there are no significant differences among the XRD patterns of the micro-arc oxidation coatings under different oxidation times. All of them exhibit the diffraction peaks of Ti, anatase-phase TiO_2, and rutile-phase TiO_2. Among them, the diffraction peak of Ti originates from the titanium substrate. In the initial stage of oxidation, the oxidation coating is thin, and X-rays can penetrate the coating and reach the substrate. In addition, due to the low oxidation intensity, the intensity of the diffraction peak of the titanium substrate is relatively high, while the peak intensities of rutile and anatase-type titanium dioxide phases are relatively weak.As the oxidation voltage increases, when it exceeds 400 V, the characteristics of the diffraction peaks of rutile and anatase in the coating become more and more significant, and the intensities of the diffraction peaks of the two increase continuously, while the diffraction peak of Ti weakens obviously. This is because the deepening of the oxidation degree leads to an increase in the thickness of the coating, thus causing a change in the phase composition[12,13]. TiO_2 mainly exists in three crystalline phases: rutile, anatase, and brookite. Among them, the rutile phase has thermodynamic stability at higher temperatures and

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is the most stable phase state; the anatase phase is formed at relatively lower temperatures and will transform into the rutile phase at temperatures higher than 800 °C. In this study, as the oxidation time is prolonged, the reaction degree gradually intensifies, and the coating surface is in an environment of high temperature and high pressure. Part of the anatase phase gradually transforms into the rutile phase. This transformation process is based on the nucleation of the rutile phase at the interface of the anatase phase, causing the structure of part of the anatase phase to undergo a phase transformation and successfully transform into the rutile phase, thus leading to an increase in the intensity of the diffraction peak of the rutile phase and a relatively weakening of the intensity of the diffraction peak of the anatase phase.

3.3 Morphology Analysis of Oxide Layer Cross Section

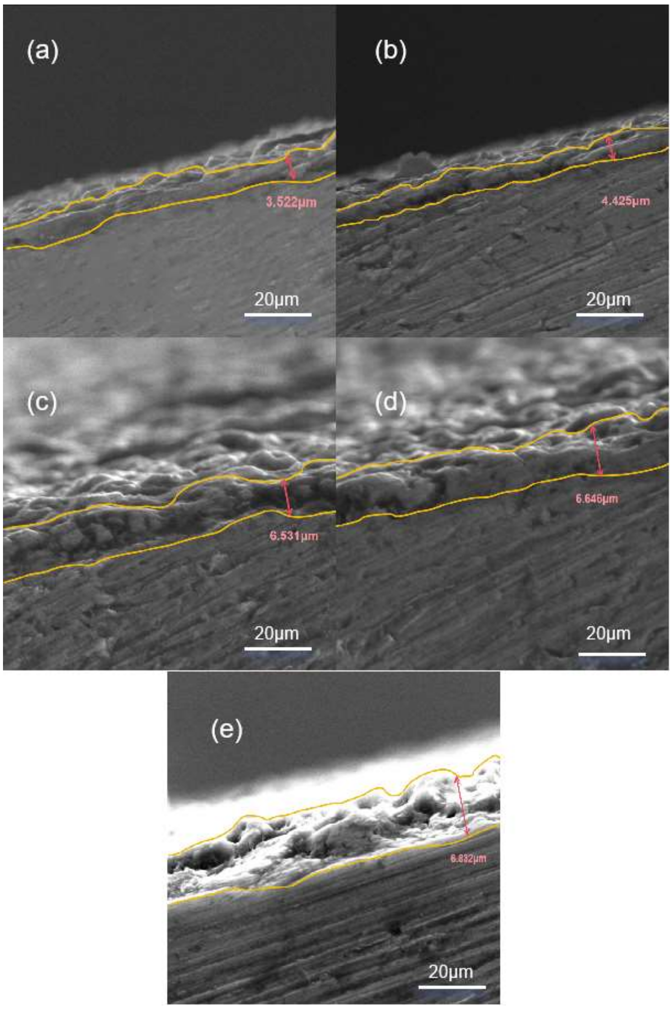

Figure 4. Morphology and thickness of oxide layer under different oxidation voltages: (a) 300 V; (b) 350 V; (c) 400 V; (d) 450 V; (e)500V

The cross section morphologies of oxide films obtained under different voltages are shown in Figure 4. As can be seen from the figure, the oxide layer thickness gradually increases with the increase of voltage. When the voltage is 350 V, the oxide layer thickness is the thinnest, which is 4.4 μm, and when the voltage reaches 470 V, the oxide layer thickness is the thickest, which is 10.7 μm. It can also be seen from the figure that when the voltage is low, the inner and outer layers of the oxide film are uneven, and there is a trend of inward and outward growth, but the oxide film has fewer defects and the coating is relatively dense. At high voltage, the inside and outside of the oxide film are relatively smooth, but there are more defects in the inside, and the higher the voltage, the more defects. This is because the growth rate of the oxide layer is slow and the thickness is thin at low pressure. When the micro-arc oxidation reaches the set time, the oxide layer still maintains the trend of inward

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and outward growth. With the increase of voltage, the growth rate of the oxide layer gradually increases, but too high voltage may cause part of the surface of the oxide layer to burn off. Due to excessive energy, the number of discharge channels increases, and the aperture increases, the internal defects of the oxide layer increase, and the structure gradually becomes loose.

3.4 Analysis of the Hydrophilicity and Roughness of the Film Layer

The hydrophilicity and hydrophobicity of the surface of biological materials affect the biological characteristics of implants, such as bacterial adhesion and cell proliferation. The hydrophilicity of the film layer is one of the key parameters for evaluating biological coatings, which directly affects the adhesion and differentiation of cells on the surface of the film layer. In practical detection, an interfacial tension measuring instrument is used to evaluate the hydrophilicity of the film layer by measuring the contact angle of the film layer. The specific operation steps are as follows: Accurately measure 3.5 μl of ultrapure water and slowly and steadily drop it onto the surface of the film layer. After the water drop has been stationary on the surface of the film layer for 5 s, use the interfacial tension measuring instrument to accurately measure the contact angle, and use this data to determine the hydrophilicity of the film layer.

Figure 5 and Figure 6 shows the contact angles and roughness of the micro-arc oxidation film layers under different voltages. Simulated saliva (SSF) was used to evaluate the wettability. The contact angles of TA2, MAO-300 V, MAO-350 V, MAO-400 V, and MAO-450 V are (89±3.1)°, (48±3.2)°, (42±2.3)°, (28±3.2)°, and (36±3.1)° respectively. Figure 3.9 shows the roughness morphology of the micro-arc oxidation film layers under different voltages. The surface roughness values are (0.548±0.023) μm, (0.664±0.027) μm, (1.045±0.024) μm, and (1.023±0.029) μm respectively. The high porosity and microstructure significantly improve the hydrophilicity and roughness of the micro-arc oxidation film layer. This enhancement is attributed to the ability of the micro-porous structure to accommodate water molecules, which improves the ability of the metal surface to come into contact with water. In addition, as the voltage increases, the content of the TiO_2 phase in the film layer also increases, which easily combines with H^+ in water to form Ti-OH groups, further increasing the hydrophilicity of the surface. The results show that MAO-400 V has the best hydrophilicity and the greatest roughness, which is conducive to the adhesion and proliferation of bacteria.

It should be noted that in the last sentence, "conducive to the adhesion and proliferation of bacteria" may need to be considered in combination with the actual application scenario. In the context of medical implants, usually, measures are taken to reduce rather than promote bacterial adhesion and proliferation. There may be a need for further clarification or correction according to the actual situation.

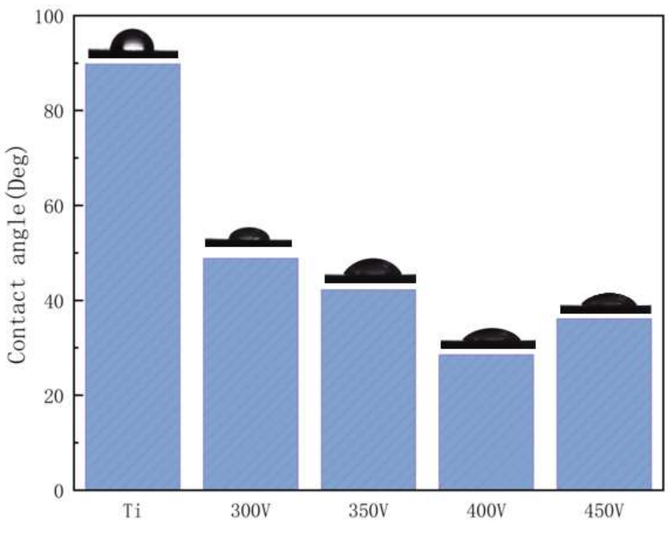

Figure 5. The contact angles of the specimens under different voltage parameters

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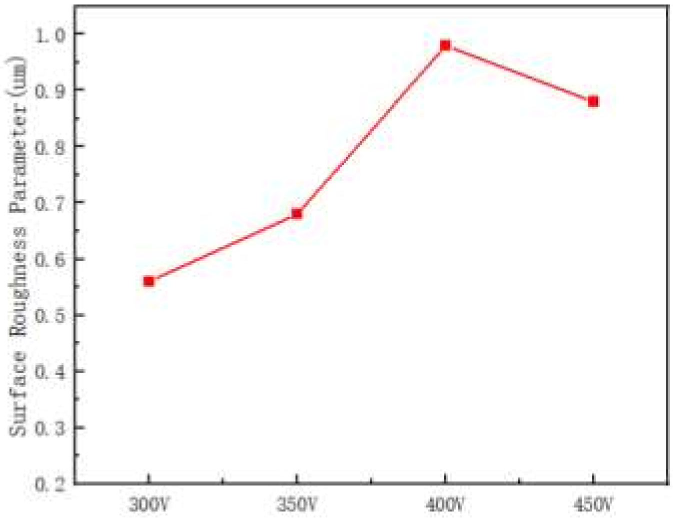

Figure 6. The roughness of the samples under different voltage parameters

3.5 Analysis of Corrosion Resistance of Oxide Layer

As shown in Figure 7 and Figure 8, it displays the polarization curves of the micro-arc oxidation film layers formed under different voltage treatments. The relevant electrochemical parameters calculated by the Tafel linear extrapolation method are listed in Table1. The influence law of the electrochemical corrosion performance of the micro-arc oxidation composite film layers in the phosphate electrolyte under different voltages is shown in Figure 7. Table 1 is the result of fitting the polarization curves.

Generally, a lower self-corrosion current density and a higher corrosion potential lead to better corrosion resistance, and vice versa. According to Table 1, after the micro-arc oxidation treatment, the self-corrosion current density of TA2 decreases by an order of magnitude, which means that the corrosion resistance of TA2 has been improved due to the micro-arc oxidation treatment, and this is consistent with the research results of Li[14] and other researchers. Therefore, the micro-arc oxidation coating can serve as an effective corrosion-resistant barrier for the TA2 alloy implant. With the increase of the voltage, the self-corrosion potential of the composite film layer first increases and then decreases. When the voltage is 400 V, the self-corrosion potential of the obtained micro-arc oxidation composite film layer is the highest, reaching -0.14 V, and the self-corrosion current density is the smallest, which is 3.80×10^{-8}, and the corrosion resistance is the best. Compared with the potential of the titanium alloy substrate (-0.57 V), the potential of the film layer after the micro-arc oxidation treatment has increased significantly, and the corrosion resistance has been enhanced. The corrosion resistance of the micro-arc oxidation layer of the titanium alloy in the phosphate system has been further improved compared with that of the titanium alloy substrate. The analysis results show that the film layer treated by MAO-400 V has a higher corrosion potential and a lower self-corrosion current, which proves that it has the best corrosion resistance. This is attributed to the increase of the applied voltage, which thickens the film layer and thus enhances its corrosion resistance. However, when the voltage is increased to 450 V, the size of the internal micro-pores of the film layer continues to expand, and at the same time, the surface of the film layer becomes rough and loose, resulting in poor corrosion resistance.

The research of Laleh et al. [15] shows that after the AZ91 magnesium alloy is treated by micro-arc oxidation, the increase in surface roughness will make it more prone to corrosion. However, the results obtained in this experiment using the TA2 alloy are inconsistent with this. This difference may be due to the fact that the corrosion resistance of the coating does not depend solely on the single factor of surface roughness, but is also affected by various factors such as chemical composition, phase composition, and defects (including pores and cracks). These defects are usually caused by the internal defects of the micro-arc oxidation coating itself, and then have a comprehensive impact on

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the corrosion resistance of the coating, ultimately leading to the difference between the results of this experiment and the research conclusions of Laleh et al.

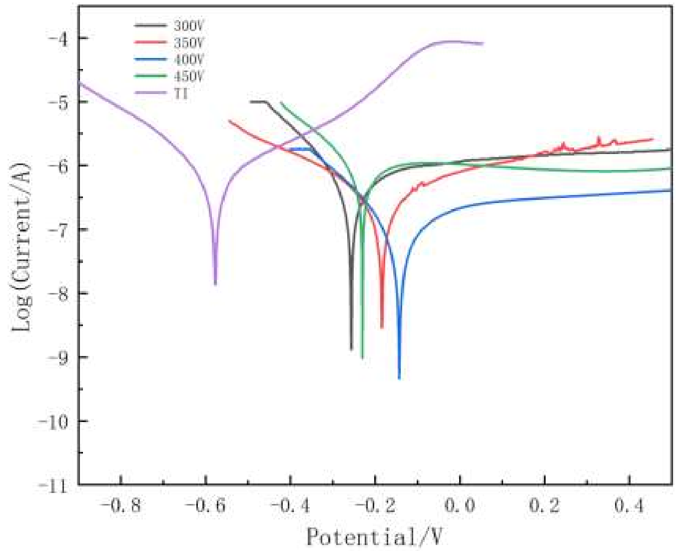

Figure 7. Polarization Curves of TiO_2 Micro-arc Oxidation Film Layers under Different Voltages

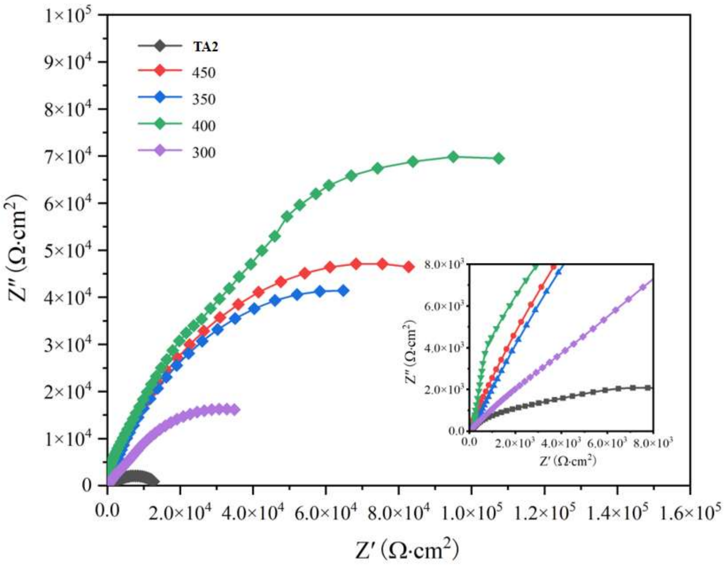

Figure 8. Nyquist curves at different oxidation voltages

Table 1. Self-corrosion potential and self-corrosion current of oxide layer under different oxidation voltages

Sample	Icorr(A/cm^2)	Ecorr(V)	OCP(V)
Ti	6.61*10^{-7}	-0.57	0.09
300V	1.78*10^{-7}	-0.26	0.12
350V	1.05*10^{-7}	-0.18	0.17
400V	3.80*10^{-8}	-0.14	0.22
450V	2.54*10^{-7}	-0.23	0.21

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4. Conclusion

This chapter analyzes and studies the characterization and properties of the surface of pure titanium (TA2) under different micro-arc oxidation process conditions.

Titanium sheets were treated by micro-arc oxidation under a constant voltage mode with different voltage parameters of 300 V, 350 V, 400 V, 450 V, and 500 V, while maintaining the same duty cycle of 5%, frequency of 500 Hz, and micro-arc oxidation time of 5 minutes.

1) After the micro-arc oxidation treatment on the pure titanium TA2 substrate, its surface exhibits a micro-porous "crater" morphology at the micron level. Through detection, the coating surface is mainly composed of Ti, O, and P elements. The study reveals that the applied voltage has a significant impact on the relevant characteristics after micro-arc oxidation. As the voltage increases, the pore size and the thickness of the film layer keep increasing. When the voltage reaches 400 V, the surface presents a uniform and dense porous morphology. At this moment, the pore size is appropriate, the film layer thickness is suitable, and the performance is relatively ideal. However, when the voltage continues to rise and exceeds 400 V to reach 450 V and 500 V, the oxide layer is damaged, and micro-cracks appear on the surface. The change trend of the porosity is that it first increases and then decreases with the increase of the applied voltage. After exceeding 400 V, the oxygen content decreases, and the porosity decreases accordingly. Through XRD analysis, it can be known that with the increase of the voltage, the rutile phase with thermal stability in the coating gradually increases.

2) After the micro-arc oxidation treatment under different voltage conditions, MAO-400 V shows unique surface characteristics. It has the smallest contact angle, which is (28±3.2)°, and the largest surface roughness, reaching 1.045μm. A smaller contact angle indicates that it has good hydrophilic properties and can quickly spread and infiltrate in a liquid environment. The surface roughness of the material is of great significance in the field of cell biology and is closely related to cell proliferation. A higher surface roughness can provide more attachment sites for cells, promoting cell adhesion and growth, and thus being conducive to improving the biocompatibility of the material, making it more advantageous in biomedical applications. In addition, MAO-400 V also demonstrates the best corrosion resistance.

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