Study on the Effect of Microarc Oxidation Voltage on the Preparation and Properties of Porous Structure on the Surface of Ti-40Nb Alloy

Meixiang Zhan

Shanghai University of Technology, Shanghai 200093, China

Abstract

Surface modification of Ti-40Nb alloys is important to enhance their biocompatibility and corrosion resistance. The surface modification of Ti-40Nb alloy by microarc oxidation under different oxidation voltages was successfully obtained with a micro-nano permeable porous structure. With the increase of oxidation voltage, the pore size gradually increases, the number of pores decreases, and the coating cross-section thickness shows the change rule of increasing and then decreasing.The formation of porous structure on the surface of Ti-40Nb alloy can significantly reduce the surface contact angle and improve the hydrophilicity of the alloy surface. In addition, the formation of porous structure also effectively improves the corrosion resistance of the alloy surface. Under the condition of oxidizing voltage of 400V, the corrosion resistance of the alloy surface is the best. Finally, the formation of porous structure on the surface of Ti-40Nb alloy can effectively reduce the elastic modulus of the surface layer of the alloy, and the preparation of the porous structure under the condition of oxidation voltage of 400V reduces its elastic modulus to 40 GPa, which is close to the range of elastic modulus of the human bone tissues (10-30 GPa), and achieves the elastic modulus required for the substitution of implants.

Keywords

Ti-40Nb Alloy; Porous Structure; Micro-arc Oxidation; Hydrophily; Biocompatibility.

1. Introduction

In the field of biomedical materials, titanium alloys have excellent corrosion resistance and biocompatibility[1-3]. Titanium alloys have good biocompatibility with human tissues, which means that they can come into contact with biological tissues without causing significant rejection. This is particularly important for implants and prostheses, which require long-term contact with surrounding tissues without causing discomfort or triggering an immune response[4-7]. In addition, titanium alloys have excellent biocompatibility, making them useful for a wide range of applications in orthopedic, dental and cardiovascular fields. Titanium alloys have excellent corrosion resistance and are resistant to corrosion and oxidation in the liquid environment of the body. This property allows titanium alloys to remain stable in the body for long periods of time without corrosion causing release or damage to the material. This is critical to the long-term reliability of implants, as they need to maintain their integrity and performance in the body to support a patient's quality of life[8-10].

Depending on the lattice structure of the material after processing and synthesis, titanium alloys are classified as α-titanium alloys, β-titanium alloys, and α+β-titanium alloys. α-titanium alloys are the first generation of titanium alloys, the most representative of which is pure titanium, and were first introduced into the field of medical artificial bone materials as replacement materials for dental implants[11-13]. However, due to its low strength, it cannot be applied to the parts of the human body

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that are subjected to large forces, so it has certain limitations in the field of artificial bone, but its good biocompatibility after implantation in the human body promotes the development of β titanium alloys and α + β titanium alloys that appeared in the subsequent period[14-16].

In order to improve the mechanical properties of pure titanium, certain alloying elements are often added to it, and thus α+β type titanium alloy was developed after α-type titanium alloy, among which Ti6Al4V alloy dominated the field of artificial bone tissues soon after its development due to its high strength and hardness compared to pure titanium and its elasticity modulus close to that of pure titanium. Moreover, Ti6Al4V alloy is currently the most widely used commercial titanium alloy, which is widely used in medical devices and high-end equipment. However, after the introduction of Al and V elements into pure titanium, while improving the mechanical properties, Al and V elements are toxic elements that are harmful to human body. Therefore, people developed Ti6Al7Nb alloy, Ti6Al7Nb alloy elastic modulus is slightly lower than Ti6Al4V alloy, the mechanical properties are also closer, and replace the V element with Nb element, Nb element has been proved to be a biosafety element, although there is still a toxic element Al exists, but it also reduces the content of the material implanted in the human body after the release of the toxic element to a certain degree, improve the The success rate of combining the material with the human body after implantation[17-18].

Beta titanium alloys are a new class of alloys that completely adopt biosafety elements. By adding niobium, zirconium and tantalum to pure titanium to replace other toxic elements, and β-type titanium alloy has a lower modulus of elasticity and is closer to human bone tissue, which has become a hot spot for researchers and scholars, but due to the high price, the application range is small at present[19].

For the parts of the human body that are subjected to large forces, it is difficult for pure titanium to meet the performance requirements, so it is essential to introduce some other elements to improve the performance, and it is of great significance to carry out surface modification of titanium alloys to ensure the mechanical properties and at the same time reduce the content of toxic elements released by the alloys in order to improve the success rate of the material after implantation[20].

The aim of this study is to investigate the effect rule of different oxidation voltages on the micro morphology of porous structure, porous coating thickness, hydrophilicity of the coating, corrosion and mechanical properties of Ti-40Nb alloy micro-arc oxidized by micro-arc oxidizing technique, which is selected to be tested in the basic electrolyte (25 g/L Na3PO4, 8 g/L KOH).

2. Experimental Methods

2.1 Test Materials

The base alloy used in this paper is Ti-40Nb alloy, which is vacuum melted in LG050 suspension melting furnace, rolled and homogenized, and then used as the base material for the preparation of porous structure in this paper.

2.2 Preparation of Porous Structures by Microarc Oxidation

The Ti-40Nb alloy was prepared as 15 mm diameter micro-arc oxidized discs using wire cutting method. Before the experiment, the samples were polished with sandpaper of different roughness (#400~#2000), and after polishing, the samples were ultrasonically cleaned with deionized water and alcohol to remove the surface contaminants, and then placed in alcohol for storage for subsequent experiments. During the test, the Ti-Nb alloy was used as the anode and the stainless steel electrolyzer as the cathode, the operation mode was constant voltage mode, the frequency was 500Hz, and the running time of the micro-arc oxidation was 5 min. During the experiment, the Ti-Nb alloy was immersed into 6L of electrolyte, and the temperature of the electrolyte was made to be at about 30℃ by the cooling device. The oxidation voltages were 300V, 400V and 500V, and the experimental samples after micro-arc oxidation were washed and dried by deionized water and then stored.

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2.3 Testing and Characterization Methods

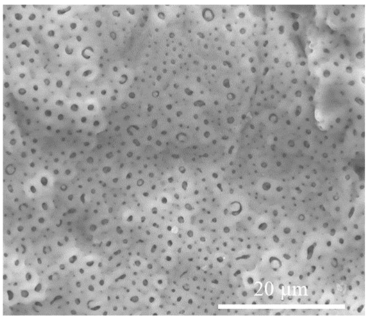
A Quanta 450 field emission ambient scanning electron microscope (SEM) was used to characterize the microstructure and morphology of the porous structure on the alloy surface. The contact angle of the alloy surface was measured by JC2000C1 interfacial tension meter. The corrosion resistance of the alloys was measured using a Chenhua CHI600E electrochemical workstation. The hardness, modulus of elasticity, and load-displacement curves of the samples were measured using a Bruker Hysitron Model TI980 nanoindentation tester.

3. Results and Analysis

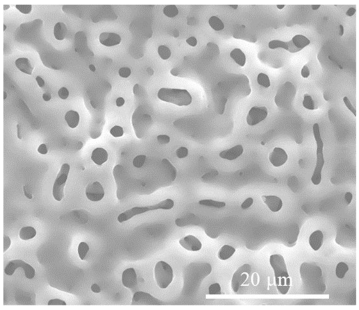
3.1 Characterization of Microarc Oxidized Porous Structure

3.1.1 Effect of Electrolyte Concentration on the Microscopic Morphology of Microarc Oxidized Porous Structures

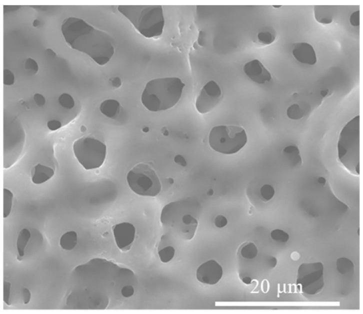
Fig. 1 shows the SEM images of the surface micro-morphology of Ti-40Nb alloy porous coatings prepared under different oxidizing voltages, respectively. As can be seen from the figure, the micro-arc oxidized porous coating is uniformly distributed with a large number of holes, showing crater-like morphology. It can be found that as the oxidation voltage increases to 400 V, the diameter of the microarc oxidized pores increases and the number of pores gradually decreases. When the oxidation voltage is increased to 500 V, the increase in pulse energy causes the number of formed holes to continue to decrease and the hole diameter to increase slightly.



(a) SEM image of porous structure with oxidizing voltage 300V



(b) SEM image of porous structure with oxidizing voltage 400V



(c) SEM image of porous structure with oxidizing voltage 500V

Fig.1 Scan of porous structure under different oxidizing voltage conditions

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3.1.2 Variation of Coating Cross-section Thickness with Oxidation Voltage

The influence of microarc oxidation voltage on the cross-sectional thickness of Ti-Nb alloy porous coating is shown in Fig. 2. As can be seen from Fig. 2, with the increase of microarc oxidation oxidation voltage, the cross-sectional thickness and growth rate of porous coatings show a trend of increasing and then decreasing. Under the condition of 300 V oxidation voltage, the cross-section thickness of porous coating prepared by micro-arc oxidation is lower, which is because the lower oxidation voltage leads to smaller ion transport rate, which makes fewer oxide ions deposited on the surface of the oxide film, and makes the cross-section thickness of porous coating smaller. When the oxidation voltage is increased to 400 V, the cross-section thickness of the porous coating is increased to 16.75 μm. The increase of the oxidation voltage leads to the increase of the pulse discharge energy, and the Ti4+ and O2- in the porous coating are rapidly transferred in the discharge channel, and the high pulse energy leads to the great increase of the plasma breakdown time and temperature, and the content of the oxides generated per unit of time on the surface of Ti-Nb alloys is greatly increased, and the higher micro-arc oxidation voltage overcomes the problem of the high oxidation voltage, and the higher oxidation voltage is used for the oxidation of porous coatings. Higher micro-arc oxidation voltage overcomes the resistance caused by the increase of equivalent resistance, and the porous coating on the surface of Ti-Nb alloy can grow rapidly. When the micro-arc oxidation voltage was increased to 500 V, the pulse energy was too large, which caused serious ablation and detachment of the external loose micro-arc oxidized porous coatings, and the thickness of the porous coating cross-section was reduced to 14.25 μm.

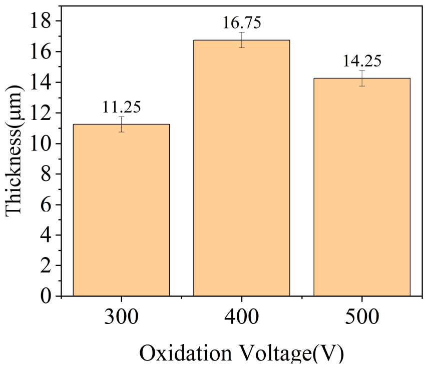

Fig. 2 Cross-sectional morphology of coatings under different oxidizing voltages

3.2 Performance Analysis of Microarc Oxidized Porous Structures

3.2.1 Coating Hydrophilicity

The hydrophilicity of the coating surface represents the ability of the titanium alloy to grow cells on its surface after implantation in the human body. The better the hydrophilicity of the coating, the better the ability of cells to attach and differentiate on the surface of human bone tissue. The contact angle of the as-cast Ti-40Nb alloy was 69.5°. When the oxidation voltage was increased to 300 V, the contact angle on the surface of Ti-40Nb alloy oxidized by micro-arc oxidation decreased to 43.0°; when the oxidation voltage was increased to 400 V, the contact angle on the surface of Ti-40Nb alloy oxidized by micro-arc oxidation decreased to 30.0°; and when the oxidation voltage was increased to 500 V, the contact angle on the surface of Ti-40Nb alloy was less than 5.0°. After preparing porous structure on the surface of the alloy by microarc oxidation, the contact angle becomes smaller, indicating that the hydrophilicity is improved. Fig. 3 shows the contact angles of the Ti-Nb alloy and the samples after microarc oxidation, from which the spreading of deionized water on the surface of the coating can be observed.

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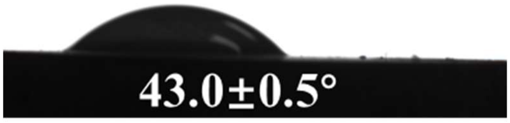
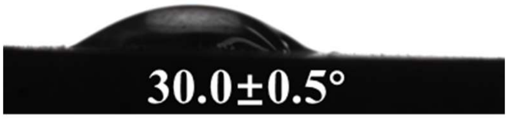
(a) Contact angle of cast Ti-40Nb



(b) Oxidizing voltage 400V contact angle of porous structure



(c) Oxidizing voltage 400V contact angle of porous structure

(d) Oxidizing voltage 400V contact angle of porous structure

Fig. 3 Contact angle of cast Ti-40Nb and alloy after micro arc oxidation

3.2.2 Corrosion Properties of Micro-arc Oxidized Porous Structures

Simulated Body Fluid (SBF) is a solution used to simulate the ionic composition and chemical properties of human body fluids for evaluating the biocompatibility of biomaterials and bone-implant interactions.SBF is the most effective solution available to simulate the human body fluid environment.SBF simulates a body fluid with a pH value of approximately 7.4.The pH can be adjusted by adjusting the HCO_3 -and HPO_4^{2}- concentrations to adjust the pH.

The corrosion properties of the Ti-40Nb alloy were tested using an electrochemical workstation, where the samples were subjected to SBF solution to measure their dynamic polarization curves. Before measuring the dynamic polarization curves, it is necessary to ensure that a stable open circuit potential (OCP) is obtained. Fig. 4 shows the polarization curves of Ti-40Nb alloy in SBF simulated body fluid under different oxidation voltage conditions. Table 4 shows the self-corrosion potentials and corrosion current densities of the polarization curves measured under the conditions of different oxidation voltages.

Corrosion potential is the potential of a metal in a corrosive environment when it reacts electrochemically with its surrounding electrolyte. It reflects the equilibrium between corrosion and protection reactions on the metal surface. The higher the general corrosion potential, the better the corrosion resistance of the material.

Corrosion current density is the current per unit area, which is related to the redox reaction of the metal in the corrosive environment. Corrosion current density is a key indicator for assessing the degree of corrosion of a metal in a particular corrosive environment. A higher corrosion current

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density usually indicates a higher corrosion rate, reflecting a stronger corrosive influence on the metal surface.

As can be seen from Table 1, the self-corrosion potential of cast Ti-40Nb is -0.531 V. After preparing a layer of porous structure on the surface of Ti-40Nb alloy by micro-arc oxidation, the self-corrosion potential (Ecorr) of the alloy surface has been effectively improved, which indicates that the corrosion resistance of the alloy surface has been well improved by plating a layer of porous structure. The corrosion resistance of the porous structure is the best when the oxidation voltage is 400V, as shown by the integrated self-corrosion potential and corrosion current density.

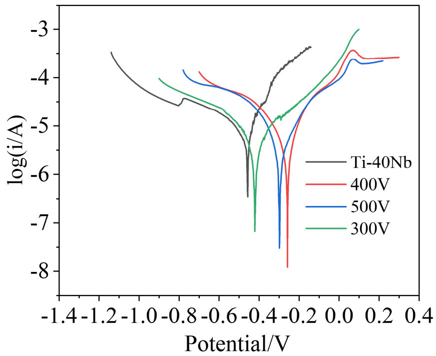

Fig. 4 Polarization curves of Ti-40Nb and porous structures after micro arc oxidation

Table 1. Polarization curve analysis results of Ti-40Nb and porous structure after micro arc oxidation

oxidation voltage	Ecorr/V	Icorr/μA•cm-2
0	-0.531	3.280
300	-0.422	5.913
400	-0.256	4.789
500	-0.297	3.971

3.2.3 Mechanical Properties of Microarc Oxidized Porous Structures

Whether the porous structure prepared by micro-arc oxidization meets the human body's demand for porous structures needs to be tested for mechanical properties. In this paper, a nanoindentation instrument was chosen to measure the modulus of elasticity and hardness of the porous structure.

The changes in the elastic modulus and hardness of the Ti-Nb alloy and a layer of porous structure prepared on the surface of the alloy by micro-arc oxidation are demonstrated in Fig. 5. It can be observed from the figure that the modulus of elasticity decreases with the formation of the porous structure on the surface of the alloy.The original modulus of elasticity of the Ti-Nb alloy is about 90 GPa, while the porous coating formed on the surface of the alloy substrate by micro-arc oxidation leads to a decrease in the modulus of elasticity. The porous structure was prepared at an oxidation voltage of 300 V, and the modulus of elasticity was reduced to 70 GPa. The porous structure was prepared at an oxidation voltage of 400 V, and the modulus of elasticity was reduced to 40 Gpa, which is close to the range of the elasticity modulus of the human bone tissue (10-30 GPa), and it has reached the elasticity modulus required for the replacement of the implant. Preparing the porous structure at an oxidizing voltage of 500 V, the elastic modulus instead rose to 60 Gpa.

In addition, although the formation of the porous structure has some effect on the hardness of the surface layer of the alloy, it basically does not affect the overall strength of the Ti-40Nb alloy. This indicates that the porous structure prepared by microarc oxidation can meet the demand of the implant in terms of elastic modulus and does not significantly affect the overall strength of the alloy.

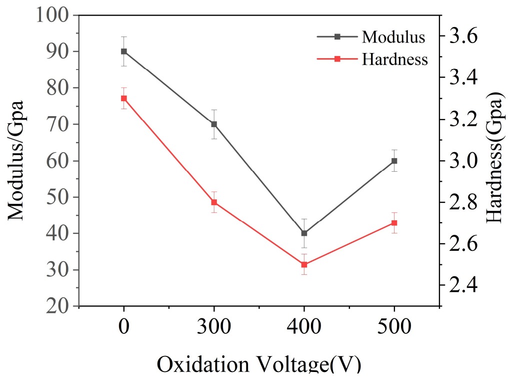

Fig. 5 Elastic modulus and hardness of Ti-40Nb alloy and porous structure after micro arc oxidation

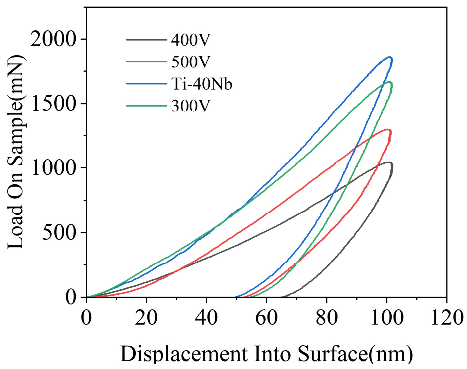

Fig. 6 Load-displacement curves of Ti-40Nb alloy and porous structure after micro arc oxidation

4. Conclusion

In this study, porous structures were prepared on the surface of Ti-40Nb alloys by micro-arc oxidation under different electrolyte concentration conditions, and in-depth studies were conducted on their microstructure morphology and properties, including hydrophilicity, corrosion properties, and mechanical properties. Several major conclusions were drawn as follows:

(1) The porous structure prepared by microarc oxidation on the surface of Ti-40Nb alloy shows small cratered pores. With the increase of oxidation voltage, the pore diameter gradually increases and the number of pores decreases. With the increase of oxidation voltage, the coating thickness shows the change rule of first increasing and then decreasing.

(2) Hydrophilicity test on the porous structure found that the contact angle was significantly reduced after the formation of porous structure on the surface of Ti-40Nb alloy, indicating that the formation of the porous coating effectively improves the hydrophilicity of the alloy surface, which is conducive to the proliferation and differentiation of cells.

(3) It was found by electrochemical corrosion test that the corrosion resistance of Ti-40Nb alloy was significantly improved after the formation of porous structure on the surface, and the alloy showed the best corrosion resistance when the oxidation voltage was 400V.

(4) The formation of porous structure can effectively reduce the elastic modulus of the surface of Ti-40Nb alloy. When the oxidation voltage is 400V, the elastic modulus of the alloy surface is reduced to 40GPa, which is close to the range of elastic modulus of human bone tissue (10-30GPa), and reaches the level of elastic modulus required for replacement of implants.

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