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PREPARATION AND INFLUENCE FACTORS OF Ti-13Nb-13Zr ALLOY SURFACE NANOTUBES

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In order to obtain uniform nanotube layer on the surface of titanium alloy to improve its corrosion resistance and biological activity, the solution of H_3PO_4 and NaF was used as electrolyte solution under the condition of 25 V DC voltage and 300 ℃ heat treatment for 2 h. Nanotube was prepared on the surface of Ti-13Nb-13Zr alloy by anodizing method. The morphology and phase composition of nanotube were characterized by scanning electron microscope (SEM) and X-ray diffractometer (XRD), respectively. The effects of oxidation time and electrolyte concentration on the formation of nanotube were investigated. The results show that the oxidation time is 120 min,1 mol/L H_3PO_4 and 0.9 wt%NaF solution as electrolyte, the morphology and shape of the nanotube are regular and the arrangement is highly ordered.

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1. Introduction

Titanium and titanium alloys have been widely used in the field of bone implant materials because of their low density, excellent processability and good adaptability to human body [1-3]. At present, Ti-6Al-4V (ELI), which contains aluminum and vanadium, is the most commonly used metal implant, but it is easy to dissolve toxic ions in the complex humoral environment of human body for a long time, which is harmful to human health. And its elastic modulus (110 GPa) is too high for human bone (5~30 GPa) [4], it is easy to cause the phenomenon of "stress shielding", resulting in the implant loosening and falling off [5-6]. Titanium alloy itself is a kind of viscous material, its wear resistance is relatively poor [7], the surface properties of titanium alloy implanted in human body can not completely adapt to the complex physiological environment of human body and have no ability of bonding with human body bone[8]. Although titanium and its alloys can naturally form a layer of TiO2 oxide film, the film can protect the titanium matrix from further corrosion in neutral and weak acid solutions, thus playing a certain role in the protection of matrix materials. However, the thickness of the natural oxide layer is too thin, only 1.5-10 nm [9]. The naturally generated oxide layer is easy to fall off and dissolve in the complex humoral environment of human body, which leads to the dissolution of metal ions and the degradation of the implant properties, which leads to the failure of implantation.

With the wide application of porous anode oxide [10], the surface modification of titanium alloy by anodic oxidation to improve its surface properties and corrosion resistance has been studied by more and more scholars [11-14]. Anodic oxidation is a process in which an oxide film is formed on the metal surface under the action of voltage and electrolyte, and the oxide film is dissolved under the action of electrolyte in the electrolyte. Kodarna et al. [15] prepared TiO2

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nanotubes on titanium surface by anodic oxidation. In order to improve the bioactivity and corrosion resistance of NiTi alloy, Wong M H et al. [16] anodized on the surface of NiTi alloy and then treated by hydrothermal treatment, it was found that the ability of inducing bone-like wollastonite in simulated body fluid was enhanced. Kim et al. [17] used anodization method to form a nanotube with an average inner diameter of about 150-200 nm and a wall thickness of about 20 nm on the Ti-xZr alloy using H_3PO_4 containing 0.5 wt% NaF as an electrolyte solution. Since the method is to grow nanotubes in situ on the surface of the alloy, the bonding strength between the nano oxide layer and the substrate is promoted.

Ti-13Nb-13Zr alloy, which contains no toxic elements and low elastic modulus, is a kind of near-β biomedical titanium alloy with good comprehensive properties [18]. In order to improve the corrosion resistance and biological activity of titanium alloy, nano-oxide layer was prepared on the surface of Ti-13Nb-13Zr alloy by anodizing method with oxidation voltage of 25 V and heat treatment at 300 ℃ for 2 h.

2. Experiment

The samples of Ti-13Nb-13Zr alloy were polished step by step with 60~1200 # sand paper, and the mixture of 1 wt%HF and 3 wt%HNO_3 volume ratio of 1:1 was used for chemical polishing for 40 s. Finally, the surface was washed with deionized water and dried to be used. A 25 V anodic oxidation voltage is provided by a DC power supply device, and 1 mol/L H_3PO_4 solution and 0.1~0.9 wt% NaF solution are used as an electrolyte solution, anodized on the surface of the polished titanium alloy for 10~180 min. Finally at the heating rate was at 5 ℃/min heated to 300 ℃ for 2 h to construct a nano-oxide layer.

The surface morphology of the sample was observed by S4800 field emission scanning electron microscope (SEM), which was produced by Hitachi Instruments Co., Ltd., Japan. The diffraction patterns were observed and analyzed by D/Max2500 X-ray diffractometer (XRD), which was produced by Japan Science Co., Ltd., and the phase analysis was carried out.

3. Results and analysis

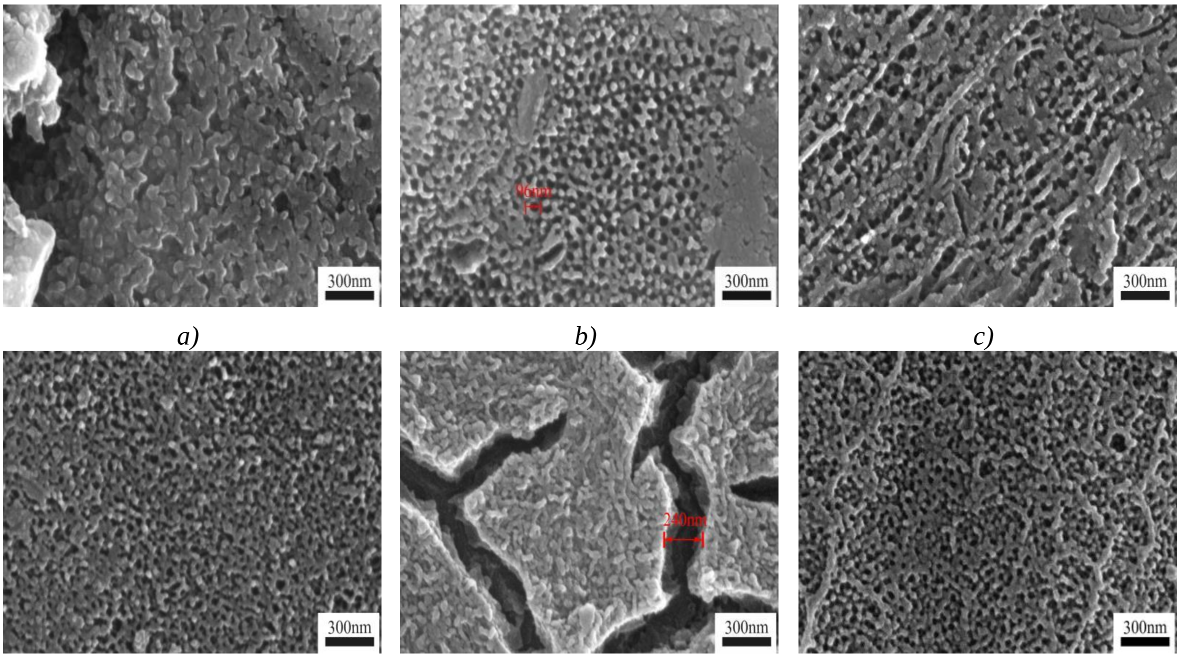
Nanotubes were grown on the surface of Ti-13Nb-13Zr alloy by anodizing process. The effects of anodic oxidation time and electrolyte concentration on the morphology and phase composition of nanotubes were investigated. The optimum process parameters for obtaining nanotube on the surface of titanium alloy were determined.

3.1. Effect of Anodizing time on Nanotubes on Ti-13Nb-13Zr Alloy Surface

Anodic oxidation is an electrochemical process in which electrolyte forms a protective layer or a modified layer on the metal surface. The main influencing factors are anodic oxidation time and electrolyte concentration. In this experiment, Ti-13Nb-13Zr alloy is used as anode, platinum sheet as cathode, 1 mol/LH_3PO_4 and 0.5 wt%NaF mixed solution as electrolyte solution, DC power supply equipment is used, the oxidation time is 10~180 min, oxidation voltage is 25 V, After heat treatment at 300 ℃ for 2 h, the growth of nanotubes was observed by SEM photos.

Fig. 1 is the SEM diagram of the nanotube under different anodizing time. As can be seen from Fig. 1, when the anodizing time is 10 min, short coarse nanoparticles and large pores appear on the surface of the alloy, the arrangement is not close, and there is no characteristic of any nanotube. When the anodic oxidation time is up to 30 min, a circular pore appears, the pore size is about 40~50 nm, the thickness of the pore wall is about 24 nm, but there is a small amount of uncorroded part on the surface of the alloy. As the oxidation time continues to increase, the electrochemical corrosion increases and local corrosion occurs. Until the anodic oxidation time is

120 min, there is a crack on the surface of the alloy with a width of about 240 nm, which is cross-penetrating, and compact agglomerated short rod aggregates appear on the surface of the alloy. When the anodizing time reaches 180 min, the surface of the alloy is completely corroded, the pore size decreases to about 36 nm, the height is ordered uniformly and the thickness of the tube wall becomes thinner to 12 nm. It shows that the increase of oxidation time, the degree of corrosion of F^- in titanium alloy in electrolyte solution increases, and the nanotubes can change from disorder to ordered arrangement.



a) *b)* *c)*

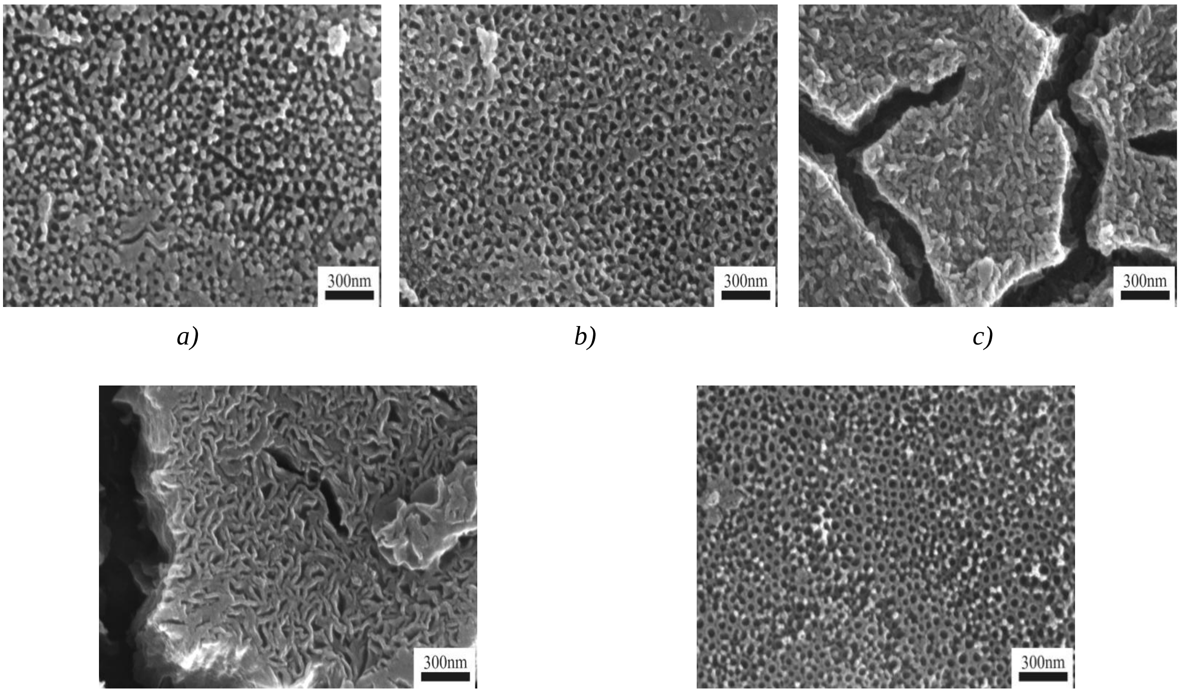
d) *e)* *f)*

Fig. 1. SEM images of nanotubes prepared at different oxidation time:
(a)10 min, (b)30 min, (c)60 min, (d)120 min, (e)150 min, (f)180 min.

3.2. Effect of electrolyte concentration on Ti-13Nb-13Zr Alloy Surface Nanotubes

Using DC power supply equipment, using 1 mol/L H_3PO_4 and 0.1% 0.9 wt%NaF as electrolyte solution, the oxidation time is 120 min, oxidation voltage is 25 V, and heat treatment is carried out at 300 ℃ for 2 h. The microstructure and phase composition of nanotube were analyzed by SEM and XRD.

Fig. 2 is the SEM diagram of nanotubes prepared in different concentrations of NaF solution. As can be seen from fig. 2, oxide layers with different morphologies appear on the surface of Ti-13Nb-13Zr alloy in different concentrations of NaF solution. When the oxidation time is constant and the electrolyte is 0.1 wt%NaF and 1 mol/L H_3PO_4, the disordered pore structure begins to appear on the surface of the alloy. When the NaF solution in the electrolyte was increased to 0.3 wt%, the morphology of the nanotubes became clear and the arrangement was relatively orderly. The pore size range was about 36 nm, and the pore wall was about 12 nm, but the pore size was different. It indicates that the F^- concentration increases, and the corrosion degree of the alloy is different under the same oxidation time. The higher the concentration, the higher the F^- diffusion, and the greater the corrosion degree of the nanopore wall and the bottom of the hole, which shows that the pore diameter increases and the pore wall becomes thinner. When the concentration of NaF solution increased to 0.5 wt%, nano-short rod aggregates appeared on the alloy surface, and large cracks appeared on the alloy surface. When the NaF solution increased from 0.5 wt% to 0.7 wt%, there were still large cracks on the alloy surface, and the agglomerated nanorods evolved into closely arranged nanorods. When the NaF solution is increased to 0.9 wt%, a highly ordered array of nanotubes appears on the surface of the alloy. The pore shape is regular, the minimum pore size is about 20 nm, the maximum pore size is about 60 nm, the wall thickness is about 12 nm. Therefore, the anodic oxidation time and electrolyte concentration affect the growth of nanotubes, synthetically. When the oxidation time is 120 min, 0.9 wt%NaF solution is the electrolyte, the morphology and shape of the nanotubes are regular and the arrangement is highly ordered.



a) *b)* *c)*

d) *e)*

Fig. 2. SEM images of nanotubes prepared in different concentration solutions of NaF: (a)0.1 wt%, (b)0.3 wt%, (c)0.5 wt%, (d)0.7 wt%, (e)0.9 wt%.

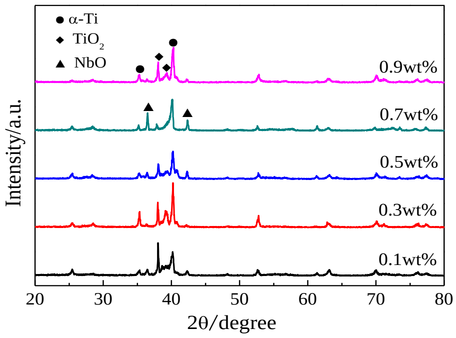


Fig. 3. XRD patterns of nanotubes prepared in different concentration solutions of NaF.

Fig. 3 is the XRD diffraction pattern of the nano-oxide layer on the surface of Ti-13Nb-13Zr alloy in different concentrations of NaF electrolyte solution. The nano-oxide layer on the surface of the alloy after anodizing mainly includes TiO_2 and niobium oxide, but there is no diffraction peak of ZrO_2, indicating that Zr is relatively stable and is not easy to be oxidized during the anodizing process. When the electrolyte concentration increased from 0.1 wt% to 0.5 wt%, the diffraction peak of TiO_2 was obviously stronger than that of NbO, indicating that TiO_2 was the main crystal phase in the oxide layer. When the electrolyte concentration is 0.7 wt%, the diffraction peak of NbO increases obviously, and the oxide layer is dominated by NbO. When the electrolyte concentration is 0.9 wt%, the diffraction peak of NbO almost disappears, and the oxide layer is mainly TiO_2.

3.3. Growth Mechanism of Nano-oxide layer on Titanium Alloy Surface

According to the literature, Al was the first metal to construct porous oxide layer on the surface by electrochemical method [19], and the other metals included Ti [20], Zr [21], Nb [22], W [23], Ta [24], Hf [25] has also been proved to be able to form a self-organized porous oxide layer on its surface under the optimal electrochemical anodizing conditions. Many scholars have studied the formation mechanism of nano-oxide tubes on different metal surfaces [26]. In acidic condition, the metal element M in titanium alloy dissolves rapidly, reacts with oxygen ion in electrolyte, and forms a dense oxide layer on the surface of the alloy. With the thickness of the oxide layer increases, the resistance of the whole circuit increases rapidly and the current decreases sharply. Because the whole oxide layer is not uniform in micro-scale, the electric field exists local concentration in the whole oxide layer. Subsequently, at the local concentration of the electric field, the oxide layer dissolves to form nano-pores. The strong soluble fluoride ion in the electrolyte reacts with the metal oxide in the oxide layer to form water-soluble metal fluoride, which can dissolve the oxide at the bottom of the nano-pore continuously. When the dissolution rate of the oxide at the bottom of the pore reaches a dynamic equilibrium with the formation rate of the surface oxide, an ordered array of nanotubes is formed. The overall anodizing reaction equation is as follows:

$$M + \frac{\mathrm{n}}{2} H_2O = MO_{\frac{\mathrm{n}}{2}} + \frac{\mathrm{n}}{2} H_2 \tag{1}$$

$$MO_{\frac{\mathrm{n}}{2}} + (\mathrm{n}+2)F^- + \mathrm{n}H^+ = \left[MF_6\right]^{2-} + \frac{\mathrm{n}}{2} H_2O \tag{2}$$

4. Conclusion

The nanotube was prepared on the surface of Ti-13Nb-13Zr alloy by anodic oxidation at 25 V oxidation voltage and heat treatment at 300 ℃ for 2 h. The effects of anodic oxidation time and electrolyte concentration on the morphology and phase composition of alloy surface nanotubes were investigated. The following conclusions have been reached:

1) According to SEM analysis, when the oxidation time is 120 min, 1 mol/LH_3PO_4 and 0.9 wt%NaF solutions as electrolytes, the morphology and shape of the nanotubes are regular and the arrangement is highly ordered.

2) According to XRD analysis, when the oxidation time is 120 min, 1 mol/LH_3PO_4 and 0.9 wt%NaF solution as electrolytes, and the oxide layer is mainly TiO2.

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