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Electrochemical Formation of Second Generation TiO_2 Nanotubes on Ti13Nb13Zr Alloy for Biomedical Applications

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The aim of this study was to obtain the second generation TiO_2 nanotubes on the Ti13Nb13Zr alloy. Anodic oxidation of the alloy under study was carried out in 1 M $(NH_4)_2SO_4$ electrolyte under voltage–time conditions of 20 V for 120 min. The morphological parameters of the obtained nanotubes of second generation such as the length (L), internal (D_i) and outer (D_o) diameter of nanotube were determined. It was found that the anodic oxidation of the Ti13Nb13Zr alloy conducted under proposed conditions allowed to obtain the single-walled nanotubes of the following geometrical parameters: the internal diameter 61 nm, outer diameter 103 nm, and the length 3.9 µm. The total surface area of the single-walled nanotubes was equal to 4.1 µm^2, and the specific surface area per cm^2 (A_s) was estimated to be 15.6 cm^2/cm^2. Formation mechanism, structure and optimal morphological parameters of the obtained single-walled nanotubes on the Ti13Nb13Zr alloy have been discussed in detail.

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1. Introduction

Surface modification of the Ti13Nb13Zr alloy expands the scope of the applicability of this alloy in medicine, particularly in the implantology [1–3]. In order to improve the biological activity of the Ti13Nb13Zr alloy and to increase its biocompatibility as well as ability to connect the bones and the implant, the surface of biomaterial should be subjected to modifications [1–4]. One of the most popular, easy-to-use electrochemical method of surface modification of titanium and its alloys is anodization. By applying the appropriate potential–current conditions, time, type and concentration of the electrolyte, the oxide layer on the surface of Ti and its alloys can be formed using this method [5–8]. Electrochemical oxidation allows to produce TiO_2 nanotubes of various parameters such as diameter, length, and wall thickness [7, 8]. This type of layers is recently used in orthopaedics, dentistry, and can also act as a drug delivery system in a precise place without oral supplementation [9, 10]. Depending on the used electrolyte the TiO_2 nanotubes belonging to one of the four generations can be produced [4, 7, 9, 10]. The purpose of the present study is to investigate the self-organized formation of nanotubular oxide layers of the Ti13Nb13Zr implant alloy in the electrolyte based on ammonia sulfate with addition of ions fluorine.

2. Experimental

The tested samples of the Ti13Nb13Zr (wt%) alloy in the form of disks were cut from the rod of 0.9 mm in diameter. The samples were ground with 1200 and 2500# grit silicon carbide paper and then polishing using OP-S suspension, sonicated for 20 min using nanopure water (Milli-Q, 18.2 MΩcm^2, < 2 ppb total organic carbon). Anodic oxidation was performed at room temperature in 1 M $(NH_4)_2SO_4$ solution with 2 wt% content of NH_4F. Value of solution pH was 5.3. The time and voltage of anodization was 120 min and 20 V, respectively. Anodization process was carried out using a Kikusui PWR800H Regulated DC Power Supply. The morphology and structure of the formed TiO_2 nanotubes layers was examined using a scanning electron microscopy with field emission HITACHI HD-2300A (FE-SEM) and the grazing incidence X-ray diffraction (GIXD) on the X'Pert Philips PW 3040/60 diffractometer operating at 30 mA and 40 kV, which was equipped with a vertical goniometer and an Eulerian cradle, respectively. The GIXD diffraction patterns were registered in 2θ range from 20° to 90° and 0.05° step for the incident angle $\alpha = 1.00°$.

3. Results and discussion

Based on preliminary review of the literature and own research in this work a new composition of the electrolyte with a higher content of fluoride ions was proposed. Addition of ions is responsible for the production of more uniform nanotubes of similar diameter as compared with non-uniform nanotubes received so far from other electrolytes with less ions F^-. In general, the mechanism with schematic diagram of TiO_2 nanotube formation in fluorine-ion based electrolytes as a result of three simultaneous processes was discussed in our previous work [1]. Figure 1 shows the GIXD pattern of the Ti13Nb13Zr alloy after anodization in 1 M $NH_4(SO_4)_2$ solution with 2 wt% NH_4F, at 20 V for 12 min. X-ray analysis in Fig. 1 revealed the presence of two phases from substrate: α-Ti and β-Ti. The diffraction pattern shows an amorphous halo which may indicate the presence of amorphous nanotubes in X-ray scale. The phenomenon of the anodic formation of oxide layers has also been reported in the literature [8].

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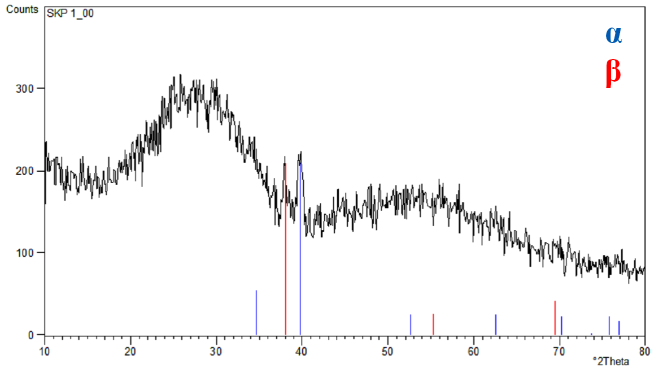

Fig. 1. GIXD pattern of Ti13Nb13Zr after anodization at 20 V for 120 min in 1 M $(NH_4)_2SO_4$ with 2 wt% NH_4F.

Based on scanning electron microscopy (SEM) images (Figs. 2 and 3) with selected areas of the Ti13Nb13Zr alloy surface after anodic oxidation, diameter and length of nanotubes were estimated. It was found that under proposed conditions single-walled TiO_2 nanotubes with an internal diameter in the range of 30–87 nm (Fig. 2a) and an outside diameter in the range of 57 to 148 nm (Fig. 2b), can be obtained.

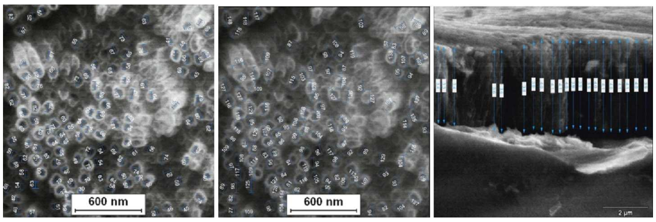

Fig. 2. The field effect SEM (FE-SEM) images with selected area to estimate: left — outer diameter, middle — internal diameter, and right — length of TiO_2 nanotubes.

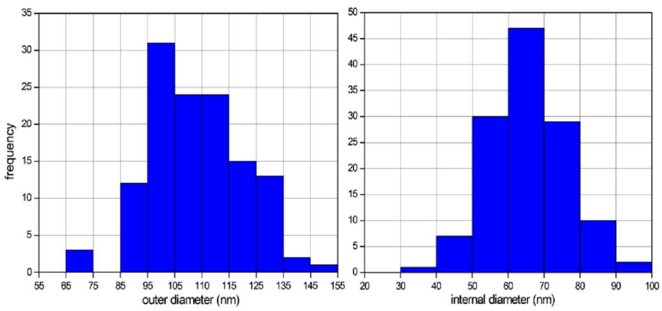

Fig. 3. Histogram of outer and internal diameter distributions of the TiO_2 nanotubes on the surface of Ti13Zr13Nb alloy after anodization at 20 V for 120 min in 1 M $(NH_4)_2SO_4$ with 2 wt% NH_4F.

Empirical distribution histograms of the diameter of the nanotubes is shown in Fig. 3a and b. The average value of the inner and outer diameter of single-walled nanotubes (SWNTs) with having regard to uncertainty of measurement is respectively $D_i = 61(11)$ nm and $D_o = 103(16)$ nm. Microscopic observation revealed that the length (L) of the obtained SWNTs changes in the range from 3.3 to 4.1 µm (Fig. 2c). The average value of the SWNT length with the consideration of measurement error is $L = 3.9(0.2)$ µm. The total area (A_i) of the nanotubes was calculated according to the following formula [8]:

$$A_i = 2\pi\left(D_0^2 - D_1^2\right) + 2\pi L(D_0 + D_1). \quad (1)$$

The first term of the above equation is associated to the areas of the two tube rings. Second term involves the areas of internal and external curved surfaces. The specific surface area (A_S) of nanotubes per cm^2 was estimated by the following term [8]:

$$A_S = nA_i. \quad (2)$$

4. Conclusion

It was found that the anodic oxidation of the Ti13Nb13Zr alloy conducted under proposed conditions allowed to obtain the single-walled nanotubes of the following geometrical parameters: the internal diameter: 61 nm, outer diameter: 103 nm, and the length: 3.9 µm. The total surface area of the SWNTs was equal to 4.1 μm^2, and the specific surface area per cm^2 (A_s) was estimated to be 15.6 cm^2/cm^2. The result of the anodization carried out in 1 M $(NH_4)_2SO_4$solution with 2 wt% content of NH_4F at room temperature at 20 V for 120 min was formation of amorphous TiO_2 SWNTs. The obtained results of FE-SEM and GIXD studies confirmed the possibility of electrochemical formation of second generation of TiO_2 nanotubes on Ti13Nb13Zr implant alloy under proposed conditions.

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