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 bone 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 TiO2 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 TiO2 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 ppb total organic carbon). Anodic oxidation was performed at room temperature in 1 M (NH₄)₂SO₄ 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 (D₁) and outer (D₂) 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 m²/cm², and the specific surface area per cm² (Aₛ) was estimated to be 15.6 cm²/cm². 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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Fig. 1. GIXD pattern of Ti13Nb13Zr after anodization at 20 V for 120 min in 1 M (NH₄)₂SO₄ with 2 wt% NH₄F.

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 TiO₂ 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 TiO₂ nanotubes.

Fig. 3. Histogram of outer and internal diameter distributions of the TiO₂ nanotubes on the surface of Ti13Zr13Nb alloy after anodization at 20 V for 120 min in 1 M (NH₄)₂SO₄ with 2 wt% NH₄F.

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 

\[ D_i = 61(11) \text{ nm and } D_o = 103(16) \text{ nm}. \]

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 \(L = 3.9(0.2) \text{ µm}\). The total area \(A_i\) of the nanotubes was calculated according to the following formula [8]:

\[ A_i = 2\pi \left( D_o^2 - D_i^2 \right) + 2\pi L(D_o + D_i). \]  

(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 cm² was estimated by the following term [8]:

\[ A_S = nA_i. \]  

(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 µm², and the specific surface area per cm² \(A_S\) was estimated to be 15.6 cm²/cm². The result of the anodization carried out in 1 M (NH₄)₂SO₄ solution with 2 wt% content of NH₄F at room temperature at 20 V for 120 min was formation of amorphous TiO₂ SWNTs. The obtained results of FE-SEM and GIXD studies confirmed the possibility of electrochemical formation of second generation of TiO₂ nanotubes on Ti13Nb13Zr implant alloy under proposed conditions.

References