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Electrochemical synthesis, corrosion behavior and cytocompatibility of Ni-Ti-O nanopores on NiTi alloy

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ABSTRACT

In the present work, we report the anodic growth of Ni-Ti-O nanopores (NPs) on NiTi alloy in ethylene glycol (EG) electrolyte containing H_2O and NaBr. It is shown that the NPs with diameter concentrated at 50–60 nm can be grown at 10 V in EG electrolyte containing 5 vol% H_2O and 0.48 M NaBr. The NP-coated NiTi alloy show lower corrosion current density compared with that of the bare NiTi alloy. In addition, the NPs possess good cytocompatibility and can even promote osteoblast spreading. Good corrosion resistance and cytocompatibility render the Ni-Ti-O NPs promising as coating of the NiTi alloy for biomedical applications.

1. Introduction

Nearly equiatomic nickel-titanium (NiTi) alloy, a special Ti alloy with unique shape memory effect and superelasticity, has been widely used in biomedical field [1,2]. Since successful fabrication of Ni-Ti-O NTs on the NiTi alloy through anodization in ethylene glycol (EG) containing H_2O and NH_4F [3], many works have demonstrated that they are promising as coatings of the NiTi alloy for biomedical applications [4–7]. For example, Desai and co-workers have shown that the Ni-Ti-O NTs do not only promote spreading and migration of endothelial cells but also depress proliferation and expression of collagen and MMP-2 of vascular smooth muscle cells, which implies the architecture is promising as a coating of NiTi-based vascular stent material [5,6]. In addition, one-end opening geometry of the NTs suggests they are more suitable as drug carriers of the NiTi alloy than previously reported coatings such as dense TiO_2 [8] and others [9,10]. The present work reports a new electrolyte system (EG + H_2O + NaBr) to fabricate Ni-Ti-O nanopores (NPs) on the NiTi alloy. Since an important concern of the NiTi alloy is its poor corrosion resistance possibly leading to ion release therefore compromising its cytocompatibility, the present work tested their corrosion behavior and cytocompatibility to preliminarily evaluate their biosafety and potential as drug carriers.

2. Materials and methods

2.1. Sample preparation and characterization

Mirror polished NiTi alloy (50.8 at.% Ni) sheets (Φ9 mm × 2 mm) were used as substrates. Anodization was conducted in a two-electrode cell with a platinum sheet as the cathode using a power supply (IT6123, ITECH, China). 100 ml of the electrolyte composed of EG, H_2O, and NaBr was used for the anodization of each sample at room temperature for 10 min. Anodization voltage and electrolyte composition were varied to investigate their influences on the anodization behavior of the NiTi alloy. Field-emission scanning electron microscopy (FE-SEM, JSM-7001F, JEOL) was used to observe the surface and cross-sectional morphologies of the anodized samples. Surface chemistry of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo).

2.2. Corrosion tests

The corrosion behavior of the samples was investigated by potentiodynamic polarization in phosphate buffered solution (PBS, pH = 7.4) at 37 °C on an electrochemical workstation (CS350, CorrTest, China) with a conventional three-electrode cell.

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A platinum foil was used as the counterpart and a saturated calomel electrode (SCE) served as the reference electrode. After soaked in PBS for 2 h, the polarization curve of each sample was recorded over a potential range of −0.6 – 0.1 V vs. open circuit potential at a scanning rate of 1 mV/s. Tafel extrapolation method was used to determine the corrosion current density (I_{corr}) of each sample.

2.3. Cytocompatibility assay

Live/dead viability/cytotoxicity kit for mammalian cells (Invitrogen) was used to evaluate the cytocompatibility of the bare NiTi alloy and anodized sample, which protocol can be found in our previous work [11]. Briefly, osteoblasts were planted on the sample surfaces at a density of 2.0×10^4 cells/cm^2 and cultured in the complete culture medium for 1, 3, and 5 days. At each time point, each sample was rinsed with PBS and incubated with the work solution of 50 μl at 37 °C for 1 h, followed by rinsing with PBS and observing on a confocal laser scanning microscopy (CLSM, C2Plus, Nikon, Japan). At least 10 random fields were captured for each sample at each time point and a typical image is shown.

3. Results

The influence of anodization parameters on the growth of NPs is summarized in Fig. S1. Under optimal condition such as anodization voltage of 10 V and EG electrolyte containing 0.48 M NaBr and 5.0 vol% H_2O, nanoporous structure can be produced (Fig. 1). Irregular NP can be seen on the outmost surface (Fig. 1(a)). After partially peeling off the NP layer, three distinct regions (Top, middle, and bottom) can be seen (Fig. 1(b)). High-magnification image of the "Top" region (Fig. 1(c)) shows the outmost surface is irregular NP layer. After peeling off the layer, ordered NPs (Fig. 1(d)) in the "Middle" region of Fig. 1(b) is exposed and its diameter concentrates at 50–60 nm (Fig. 1(h)). In the high-magnification image of the "Bottom" region (Fig. 1(e)), where NP layer is completely removed, nanopits underneath the NPs can be observed. Low-magnification cross-sectional SEM image (Fig. 1(f)) shows the NP length is 2.4 μm and its high-magnification image (Fig. 1(g)) clearly shows its nanoporous structure.

Fig. 2 shows the polarization curves of the bare NiTi alloy and the anodized sample and their respective I_{corr} was acquired by Tafel extrapolation method. Obviously, the I_{corr} of the bare NiTi alloy is more than two times of that anodized sample, which implies the corrosion resistance of the NiTi alloy is improved after anodization.

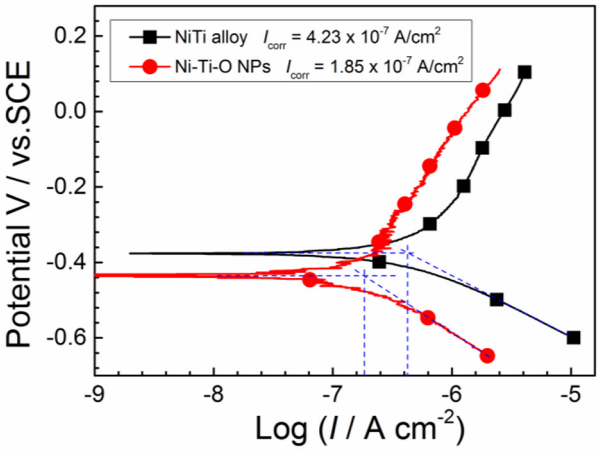

Fig. 2. Polarization curves of the NiTi alloy and anodized sample (Ni-Ti-O NPs). The sample was anodized at 10 V in EG electrolyte containing 5.0 vol% H_2O and 0.48 M NaBr.

Fig. 3 shows the fluorescence images of osteoblasts cultured on the surfaces of the bare NiTi alloy and anodized sample for 1, 3, and 5 days. Cell numbers on both of them increase with culturing time. After culturing for 5 days, nearly their entire surfaces are covered with the cells. Another phenomenon is that the cells cultured on the surface of Ni-Ti-O NPs spread better, as manifested by larger spreading area of individual cell, than that on bare NiTi alloy.

4. Discussion

The present work shows, for the first time, ordered Ni-Ti-O NPs can be generated in EG electrolyte containing small fractions of H_2O and NaBr by anodization. Typically, if there is no Br^- in the electrolyte, the constituent elements of the NiTi alloy may be oxidized to TiO_2 and NiO through the following reactions [12]:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^- \quad (1)$$

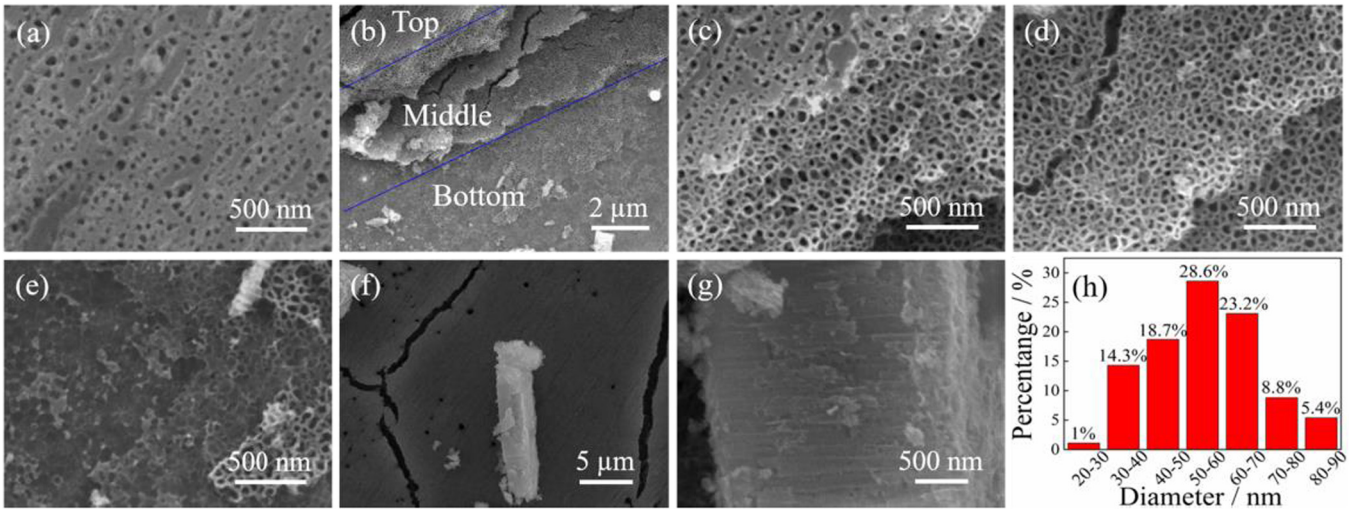

Fig. 1. Surface and cross-sectional SEM images of the sample anodized at 10 V in EG electrolyte containing 5.0 vol% H_2O and 0.48 M NaBr. (a) Surface SEM image of the sample. (b) Surface SEM image of the sample after partially peeling off the NP layer by scratching. (c)-(e) High-magnification SEM images correspond to "Top", "Middle", and "Bottom" regions in (b) respectively. (f) and (g) Low- and high- magnification cross-sectional SEM images of the NP layer. (h) Histogram of the distribution of NP diameter acquired from (d).