



Ni-doped TiO₂ nanotube arrays on shape memory alloy

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ABSTRACT

Self-organized Ni–Ti–O nanotube arrays were fabricated through a direct anodization of NiTi shape memory alloy in glycerol-based electrolyte. The growth of Ni-doped TiO₂ nanotube arrays was mainly affected by anodization voltage and temperature. Higher anodization voltage facilitated the growth of uniform nanotube arrays. Large-area open-ended Ni–Ti–O nanotube arrays could form on the surface of the shape memory alloy under a higher anodization temperature. The oxide nanotubes had a gradually changed composition along the growth direction of the nanotube and presented a thermal stability up to 400 °C. The nanotubular oxide demonstrated a much better hydrophilic behavior than that of the traditional oxide layer grown on NiTi substrate through air oxidation. The successful fabrication of Ni-doped TiO₂ nanotube arrays here makes it feasible to further explore excellent physical and chemical as well as biomedical properties of the nanotube-modified surfaces of the NiTi shape memory alloy.

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1. Introduction

As one of the most important shape memory materials showing remarkable shape memory effect and superelasticity, nickel-titanium alloys, especially the equiatomic Ni–Ti alloy known as Nitinol, has been successfully used in medical and clinical applications such as dental and orthopedics as well as cardiovascular areas [1–3]. Due to a toxic nature of Ni element that usually causes allergic responses, the release of Ni from NiTi-based implants or devices in human body has become one of the big issues that highly demand a surface modification of the NiTi alloy through various methods including air oxidation, ion implantation, hydroxyapatite coating, chemical etching, anodization, etc. [4–6].

In comparison with other surface modification methods, anodization process has shown its great capability in fabricating controllable protective layers such as dense and porous oxide films [7–11]. Cheng et al. fabricated a dense oxide layer on the Nitinol surface in methanol and found a decreased release of Ni element [12]. Huang et al. proved that anodization in diluted hydrogen fluoride solution could significantly increase the surface roughness and corrosion resistance of NiTi film [13]. The same findings were found with the acetic acid system and high voltage pulse anodization as well as AC anodization [14–17].

As high-aspect-ratio oxide nanotubes are expected to be peculiar for various kinds of applications including drug delivery and diffusion barrier, it is highly desirable to grow oxide nanotubes on shape memory alloys. TiO₂ nanotubular layer was grown after anodization of a TiO₂ layer produced on the NiTi surface through oxygen plasma immersion ion implantation [18]. And in a recent work, Kim et al. fabricated Ni–Ti–O nanotubes on NiTi foils through a high voltage anodization process. Good pseudocapacitor behavior was found with the crystallized nanotubes [19]. Here, we report a direct anodic growth of Ni-doped TiO₂ nanotubes on NiTi shape memory alloy through using glycerol-based electrolyte as the anodization media. A moderate thermal stability and good hydrophilicity were found with the Ni-doped TiO₂ nanotubes.

2. Experimental

Biomedical NiTi (nominal composition: 50.8 at.% Ni) plates with a size of 10 mm × 10 mm × 1 mm were grinded and polished with emery papers, and then ultrasonically cleaned with absolute alcohol. Finally, they were rinsed with deionized water and dried in N₂ stream. Electrochemical anodization was carried out with a DC voltage stabilizer, which provided an output voltage ranging from 15 V to 30 V. Non-aqueous electrolyte of 5% ethylene glycol/glycerol containing 0.15 M (NH₄)₂SO₄ and 0.2 M NH₄F was used as the anodization media [20]. The anodization was conducted at temperatures ranging from 20 °C to 30 °C. After 1.5 h of anodization the anodized samples were taken out of the anodization media and ultrasonically cleaned in water. They were then dried with N₂ for

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further treatment or surface examination. To examine the thermal stability of the oxide layer, some of the as-anodized samples were also heat-treated at elevated temperatures (up to 500 °C) for 1 h in air (the heating rate was about 10 °C/min). For comparison, NiTi substrate grinded and polished with the same emery papers was also oxidized at 400 °C for 30 min in air to grow traditional dense oxide layer on the shape memory alloy.

Surface morphologies of the as-anodized samples and heat-treated samples were investigated with scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis (EDXA). The operating voltage for the SEM observation was 5 kV. Phase structures of the as-anodized samples as well as the alloy substrate were investigated with X-ray diffraction (XRD, D/max 2550 V). Surface compositions and composition distribution along the depth of the cross-section were characterized with X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos). The composition of a bare NiTi plate grinded and polished with emery papers was also characterized by XPS. To evaluate the wetting behaviour, water contact angles of various samples were tested in an OCA 20 system using 3 μ l water drops.

3. Results and discussion

3.1. Microstructures

We have tried $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{F}$ based solution to anodize the shape memory alloy but only obtained irregular and porous oxides. Considering many other anodization medias reported in the previous literatures we believe that traditional anodization media was not favorable for a growth of Ni–Ti–O (NTO) nanotubes on shape memory alloy. Thus, in the present work, we use the glycerol-based electrolyte (5% ethylene glycol/glycerol containing 0.15 M $(\text{NH}_4)_2\text{SO}_4$ and 0.2 M NH_4F) for anodic growth of oxide nanotubes on NiTi shape memory alloy.

Fig. 1 shows the variation of anodic current density with anodization time and anodization voltage (The anodization temperature was 30 °C). Fig. 2 presents surface morphologies and cross

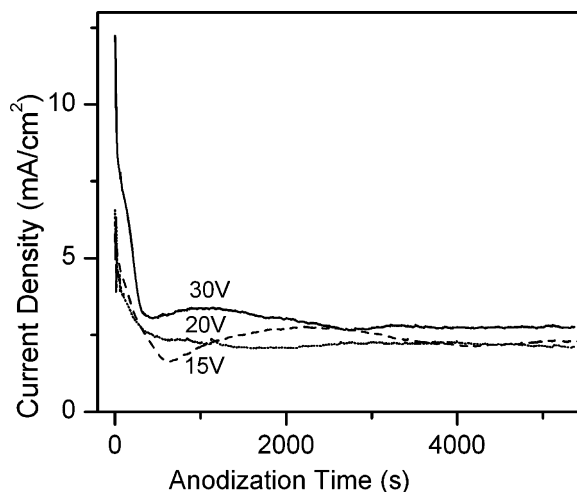


Fig. 1. Current density vs. time curve of the samples anodized at different voltages. The anodization temperature was 30 °C.

section images of the anodic oxides grown at 15 V and 20 V. For the sample under anodized at 15 V, a nanoporous layer with a thickness above 50 nm could be formed on top of the NiTi substrate. At 20 V, nanotubes with a diameter less than 40 nm and length of about 250 nm could be formed. However, the top surface of the nanotubes was often covered with irregular oxides. With increase of the anodization voltage to 30 V, large-area open-ended nanotube arrays could be observed on top of the NiTi alloy (Fig. 3). The nanotubes had a diameter around 50 nm and a length of 350 nm. Our investigations indicate that anodization temperature could also affect the formation and growth of nanotube arrays. For the sample fabricated at lower anodization temperature of 20 °C, nanotube arrays could be covered with a thin top layer of nanoporous oxide (Fig. 4).

During the anodization process a competition between formation and dissolution of the oxides always took place [21]. If

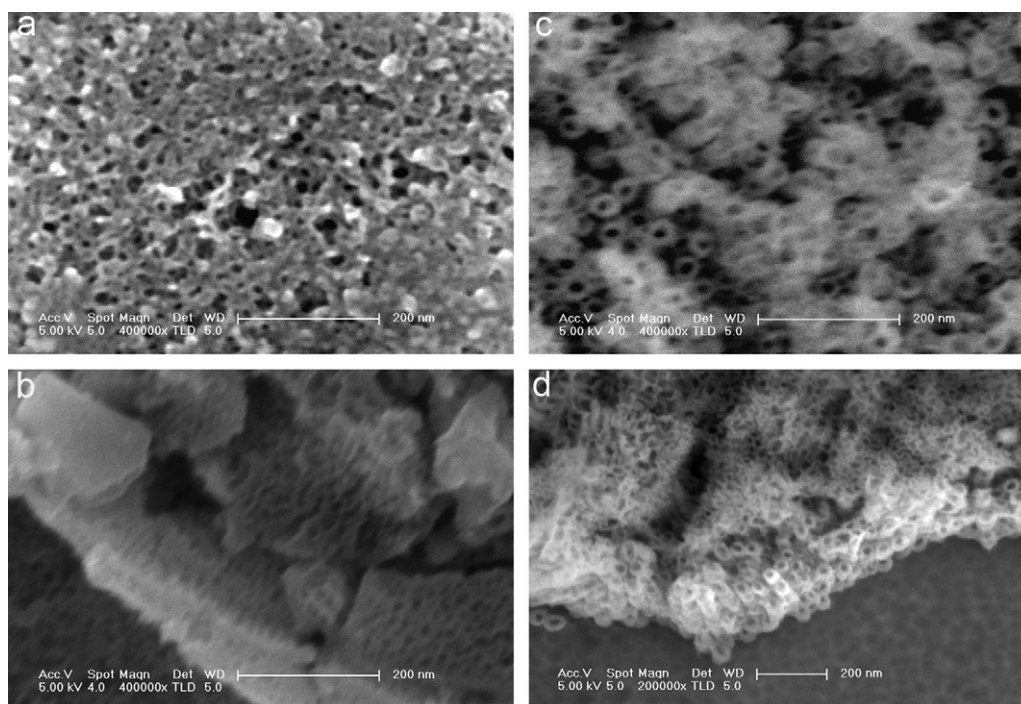


Fig. 2. Top surface and cross section images of the samples fabricated at different anodization voltage. (a and b) 15 V and (c and d) 20 V. The anodization temperature was 30 °C.

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