



Preparation and properties of titanium oxide film on NiTi alloy by micro-arc oxidation

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ABSTRACT

Titanium oxide ceramic coatings were prepared by micro-arc oxidation (MAO) in galvanostatic regime on biomedical NiTi alloy in H_3PO_4 electrolyte using DC power supply. The surface of the coating exhibited a typical MAO porous and rough structure. The XPS analysis indicated that the coatings were mainly consisted of O, Ti, P, and a little amount of Ni, and the concentration of Ni was greatly reduced compared to that of the NiTi substrate. The TF-XRD analysis revealed that MAO coating was composed of amorphous titanium oxide. The coatings were tightly adhesive to the substrates with the bonding strength more than 45 MPa, which was suitable for medical applications. The curves of potentiodynamic polarization indicated that the corrosion resistance of NiTi alloy was significantly improved due to titanium oxide formation on NiTi alloy by MAO.

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1. Introduction

NiTi alloys have been introduced for biomedical applications in the last two decades due to their unique shape memory effect, excellent super-elasticity and good resistance to fatigue and corrosion [1]. Up to now, NiTi alloys have already been used as bone fracture fixation plates and nails, vascular, non-vascular stenting and so on in the orthodontics, cardiovascular and orthopedics field [2]. However, NiTi alloy is one kind of bioinert material and exhibits poor osteoinductive properties when implanted in a human body [3]. Furthermore, the high Ni content in the alloy is of great concern with regards to its biocompatibility because the Ni releasing is a potential danger, which could induce toxic and allergic responses [4,5]. To reduce the Ni content on the surface of the NiTi alloy and improve its corrosion resistance, various surface modification technologies have been employed including thermal oxidation [6], plasma-spraying [7], laser surface treatment [8], sol-gel method [9], anodic oxidation [10,11] and plasma immersion ion implantation [12,13] etc. These processes, each with its own merits and limitation, are different in complexity and in the characteristics of the surface layer formed.

The MAO technique attracted more attentions to prepare oxide ceramic coatings on the surface of valve metals, such as Ti, Al, Mg and their alloys [14–16]. The MAO coatings on Ti and Ti–6Al–4V can offer a combination of good corrosion resistance and high bonding strength between the substrates and coatings. Therefore, MAO method has been considered as an available technique on biomedical metal surface modification, especially on Ti and its alloys to form TiO_2 coating. Unfortunately, owing to the high Ni content in NiTi, it is difficult to prepare ceramic coating on the surface of NiTi by MAO process. In recent years, the Al_2O_3 coatings on NiTi alloy have been successfully prepared by MAO in our group, which exhibited good corrosion resistance and bonding strength [17–20]. It is well known that TiO_2 is the most biocompatible biomaterials compared to other ceramic materials such as Al_2O_3 and ZrO_2 . So TiO_2 film preparation on NiTi alloy by MAO is worth of study taking into the account of the efficiency that MAO performs on NiTi alloy.

In this study, we successfully prepared titanium oxide ceramic coating on NiTi alloy in H_3PO_4 electrolyte using DC power supply by MAO. The microstructure and composition of the coatings were investigated by means of SEM, XPS and TF-XRD. The corrosion resistance and the bonding strength of the coatings were also evaluated.

2. Experimental details

Commercially available NiTi alloy (nominal composition: 50.8 at.% Ni) rectangular samples with the size of 10 mm × 10 mm × 1 mm were used as the substrate materials.

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Table 1
Chemical component of Hank's solution.

Components	Concentration (g/l)
NaCl	8
KCl	0.4
MgSO ₄ ·7H ₂ O	0.06
KH ₂ PO ₄	0.06
Na ₂ HPO ₄ ·2H ₂ O	0.06
NaHCO ₃	0.35
Glucose	1
MgCl·6H ₂ O	0.1
CaCl ₂	0.14

The samples were polished with SiC sandpaper down to 800 #, and then ultrasonically cleaned with acetone 10 min and distilled water 10 min. A direct current power supply was employed for MAO coatings preparation on NiTi alloy. The NiTi alloy samples were used as anode while with the wall of the stainless steel container as the cathode. The MAO process was operated in H₃PO₄ electrolyte with a constant current density 10 A/dm². During the experiment process, the electrolyte solution was stirred and cooled below 20 °C. Hydrothermal process was operated in a stainless steel cell filled with 70% distilled water at 250 °C for 4 h. After the treatment, the samples were rinsed with distilled water and dried in air at room temperature.

The surface and cross-sectional morphologies of the samples were observed by a scanning electron microscopy (SEM, FEI, QUANTA-200F). The phase composition of the coated samples was analyzed by thin-film X-ray diffraction (TF-XRD, Philip X'Pert) using a Cu K α radiation with a glancing angle of 5°. The chemical composition in the coatings was detected by an X-ray Photoelectron spectroscopy (XPS, PHI5700, America Physical Electronics) with Al K α X-ray source (1486.6 eV). Survey scans were measured for element species on the surface of the MAO coating over a binding energy range of 0–1100 eV using a constant pass-energy 187.85 eV. The high resolution XPS spectra were recorded using a constant pass-energy of 29.35 eV for elemental quantification. Elemental quantification was calculated from the integrated peak areas by employing instrumental sensitivity factors as supplied by the manufacturer and expressed in atomic percentage. The bonding strength of the coating was determined using a direct pull-off test according to the ASTM C-633 method by an instron-5569 testing machine. Both sides of substrates (with one side treated by MAO) were attached to cylindrical stainless steel jigs 10 mm in diameter and 15 mm in length by using the epoxy glue.

The corrosion resistance of the coated and uncoated samples was evaluated by potentiodynamic polarization test through CHI604 electrochemical analyzer (Shanghai, China) in Hank's solution (pH 7.4, the composition given in Table 1) at 37 °C. The electrochemical measurement was conducted using a conventional three electrodes electrochemical cell with a saturated calomel electrode (SCE) as the reference and Pt foil as the auxiliary electrode. The samples with the area of 1 cm² exposing to the Hank's solution served as the working electrode. Prior to the beginning of the potentiodynamic polarization test, the samples were kept in the solution for 30 min to allow the open circuit potential to become stable. The polarization scan continued in the anodic direction with a potential scan rate of 0.167 mV/s.

3. Results and discussion

3.1. Voltage–time response

The typical voltage–time response during the MAO process in constant current density 10 A/dm² on NiTi alloy samples is shown

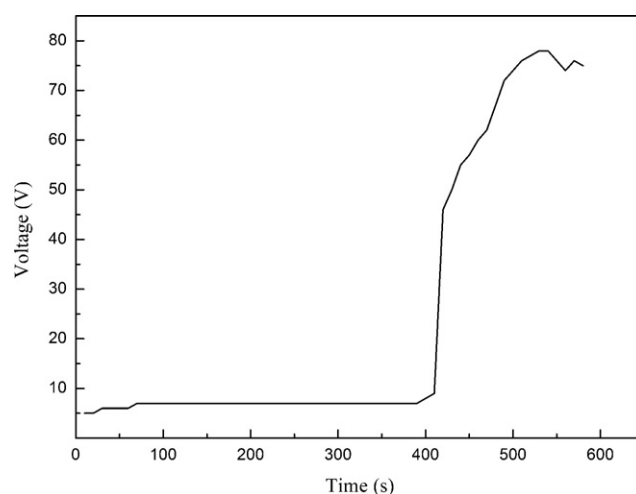


Fig. 1. The voltage–time response during the micro-arc oxidation process in galvanostatic regime.

in Fig. 1. Obviously, four regions can be found in this curve. In the first stage the voltage keeps stable at 6–7 V during 380 s, and then the voltage increases to 52 V within 10 s. The voltage–time response during the MAO process indicates that NiTi alloys undergo a relatively long barrier layer formation time, which is the evidence that NiTi alloys is difficult to modify by MAO process.

When the voltage reaches 52 V, dielectric breakdown occurs and visible discharge sparks can be found on the surface of the NiTi alloy samples. After this stage, the voltage increase rate begins to slow down, and the discharge sparks become brighter and brighter with decreasing of the spark density and increasing of the spark size. With the treatment time further increasing, the voltage slowly increases up to 78 V, and then an oscillating decrease follows with the unstable discharge sparks.

From Fig. 1, it can also be seen that the voltage–time response during the NiTi MAO process shows a significantly difference from the traditional valve metals MAO process [21], especially at the initial stage of the MAO process, the NiTi alloy undergoes a relatively long anodic oxidation time compared to valve metals. It indicates that in this selected electrolyte the much longer time is needed for NiTi alloy to form uniform and steady barrier layer at the initial stage of the MAO process compared to the traditional valve metals. Further more, this phenomenon is also different from our previous study when we employ NaAlO₂ as the MAO electrolyte to treat NiTi alloy [22], and in that electrolyte the barrier layer can be formed through the Al(OH)₃ and take less time at the anodic oxidation stage. All these differences indicate that the MAO mechanism of the NiTi alloy in H₃PO₄ electrolyte is different from that of the traditional valve metal and also different form NiTi alloy in NaAlO₂ electrolyte.

3.2. Surface and cross-section morphologies

Fig. 2 shows the surface morphologies of the MAO coatings on NiTi alloy treated for different time after the spark discharge happened. It is observed that the coating surface exhibits a typical MAO rough and multiporous structure at different treatment time. The size of the pores in coatings tends to increase with increasing of the treatment time before 90 s, however, decreases at 120 s. As illustrated in Fig. 2(a–c), some smaller pores are formed on the inner wall of the bigger craters, and the porosity of the coatings is decreased with increasing of the treatment time. When the treatment time prolongs to 120 s, the MAO coating becomes much more rough and irregular (Fig. 2(d)), which is resulted from the unstable discharge sparks described in Section 3.1. As a bone implant mate-

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