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# Microstructure and corrosion resistance behavior of ceramic coatings on biomedical NiTi alloy prepared by micro-arc oxidation

J.L. Xu [a], F. Liu [a], F.P. Wang [b,*], D.Z. Yu [c], L.C. Zhao [a]

[a] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China
[b] Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, PR China
[c] Stomatological Medicine Center, Harbin Institute of Technology, Harbin 150001, PR China

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ABSTRACT

In this paper, ceramic coatings were prepared on biomedical NiTi alloys by micro-arc oxidation (MAO) in constant voltage mode. The current density–time response was recorded during the MAO process. The microstructure, element distribution and phase composition of the coatings prepared at different MAO treatment times were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectrometer (EDS), thin-film X-ray diffraction (TF-XRD) and X-ray photoelectron spectroscopy (XPS). The corrosion behavior of the coatings in 0.9% NaCl solution was evaluated by the potentiodynamic polarization test. It is found that the coatings become more compact with increasing the MAO treatment time, and the growth rate of coating decreases. The results of TF-XRD, EDS and XPS indicate that the coatings are composed of a large amount of γ-$Al_2O_3$ and a little α-$Al_2O_3$, $TiO_2$ and $Ni_2O_3$. The Ni content of the coatings is about 3 at.%, which is greatly lower than that of NiTi substrate. The bonding strength of coating-substrate is higher than 40 MPa for all the samples in this study. The corrosion resistance of the coatings is about two orders of magnitude higher than that of the uncoated NiTi alloy.



## 1. Introduction

The almost equiatomic NiTi alloy is widely used in numerous biomedical applications (orthodontics, cardiovascular, orthopaedics, etc.), for its distinctive thermomechanical and mechanical properties, such as shape memory effect, super-elasticity, low elastic modulus and high damping capacity, etc. [1]. However, NiTi alloy is still a controversial biomaterial because of its high Ni content which can trigger the risk of allergy and adverse reactions when its ion releases into the human body [2,3]. In order to reduce the amount of Ni on the surface layer and improve the corrosion resistance of the NiTi alloy, many surface modification techniques have been employed in previous literature [4–7], among which anodic oxidation is one of the most popular methods [8–10]. Recently, micro-arc oxidation (MAO), derived from conventional anodic oxidation, has attracted more attention in virtue of its convenience and effectiveness to prepare oxide ceramic coatings with porous structure on the surface of Ti, Al, Mg and their alloys [11–13]. MAO treatment can remarkably enhance surface properties of metals, such as wear resistance, corrosion resistance and especial interface bonding to substrate in comparison with the normal anodic oxidation treatment. Biomedical Ti and Ti–6Al–4V alloy treated by MAO to improve their corrosion resistance and bioactivity have been studied a lot [14–16]. Unfortunately, to our knowledge, studies on the MAO technique to improve the corrosion resistance of NiTi alloy have not been reported in literature. In this work, ceramic coatings were prepared on NiTi alloy by the MAO method. The microstructure, composition and bonding strength of the ceramic coatings prepared by MAO at different treatment times were studied, and the corrosion resistance behavior of the coatings in 0.9% NaCl solution was also evaluated.

## 2. Experimental

### 2.1. Sample preparation

Commercial NiTi alloy (50.8 at.% Ni, in austenitic phase) samples with dimensions of 15 mm × 15 mm × 2 mm were successively polished with SiC paper down to 800#, and then ultrasonically cleaned in acetone and distilled water, respectively. The micro-arc oxidation process was conducted on a 20-kW homemade pulsed bipolar power supply. The NiTi alloy samples were used as the anode, while the wall of the stainless steel container as the cathode. An aqueous electrolyte was prepared from a solution of sodium

* Corresponding author at: Department of Applied Chemistry, Harbin Institute of Technology, Box 414, Harbin 150001, PR China. Tel.: +86 451 86418409; fax: +86 451 86413707.
*E-mail address:* xjl505@hit.edu.cn (F.P. Wang).

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aluminate and sodium hypophosphite with the analytically pure at concentration of 0.15 M and 0.01 M, respectively. The samples were treated in the electrolyte with constant voltage 400 V for 10–90 min. During the experiment process, the electrolyte solution was stirred and cooled below 35 °C. Coated samples were flushed with water after the treatment and dried in air at room temperature.

### 2.2. Microstructure characterization

The surface and cross-section morphologies of the samples were observed by a scanning electron microscopy (SEM, S-4800, Hitachi, Co., Japan). The elemental distribution was measured by an energy dispersive X-ray spectrometer (EDS, Oxford Model 7537, England). The phase composition of the samples was analyzed by thin-film X-ray diffraction (TF-XRD, Philip X' Pert, Holland) using a Cu Kα radiation with a glancing angle of 1°. The oxidation states of the elements in the coatings were determined by an X-ray photoelectron spectroscopy (XPS, PHI 5700, America Physical Electronics). The thickness of coatings was measured through the cross-section SEM morphologies. The average thickness of the coatings was obtained from 10 measurements at different positions.

### 2.3. Bonding strength test

The bonding strength between the coating and the substrate was investigated by the direct pull-off method (modified ASTM C-633). Both sides of the sample (one side was coated, the other was uncoated) were attached to cylindrical stainless steel rods 10 mm in diameter and 15 in length using epoxy resin. The pull-off test was carried out on Instron-5569 stretcher and tensile load was applied with a cross-head speed of 1 mm/min until fracture occurred. For each kind of coating prepared at different treatment time, five samples were used and the mean tensile bonding strength was calculated from the fracture load and surface area ($\pi \times 5^2$ mm$^2$).

### 2.4. Corrosion resistance

The corrosion behavior of the coated and uncoated samples in 0.9% NaCl solution was evaluated by potentiodynamic polarization test through CHI604 electrochemical analyzer (Shanghai, China). The electrochemical measurement was conducted using a conventional three electrodes electrochemical cell with a saturated calomel electrode (SCE) as the reference, a Pt foil as the auxiliary electrode, and the samples with the area of 1 cm$^2$ as the working electrode. Prior to the beginning of the potentiodynamic polarization test, the samples were kept in the solution for 0.5 h to obtain a steady value. The polarization scan continued in the anodic direction with a potential scan rate of 0.167 mV/s.

## 3. Results and discussion

### 3.1. Current density–time response

The typical current density–time response during the micro-arc oxidation treatment process in constant voltage mode on NiTi alloy is shown in Fig. 1, in which the voltage is 400 V. Furthermore, the current density–time response is highly reproducible in different voltages except that final current densities are not the same. It could be seen that the current density increases rapidly at the beginning, but after about 1 min it decreases almost with the same rapidity and then decreases slowly with increasing the treatment time after 4 min. It is similar to the current density–time response of the Ti–6Al–4V treated by MAO in constant voltage mode except the much larger current density in the initial stage [17], which may result from the high Ni content on the surface of NiTi alloy.

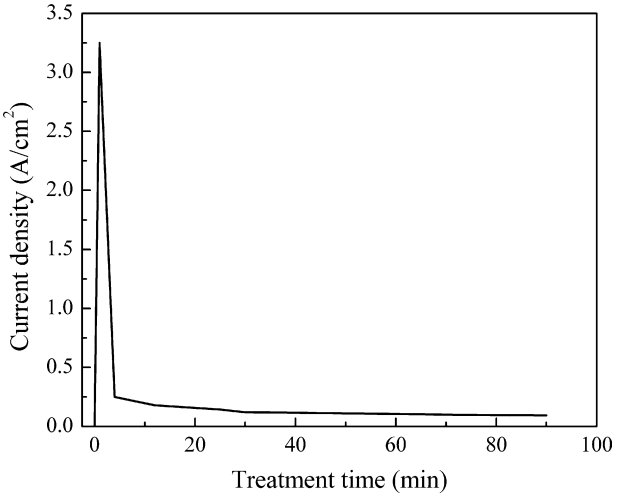


**Fig. 1.** Current density vs. time response during the micro-arc oxidation treatment in constant voltage mode on NiTi alloy.

### 3.2. Thickness of the coatings

The thickness of coatings prepared on NiTi alloy by MAO as a function of oxidation duration is given in Fig. 2. It could be noted that the thickness of the coatings is increased with increasing the treatment time, while the growth rate is decreased. In addition, the color of the coatings changes from brown gray to the jet black with increasing the treatment time.

With increasing the treatment time, the thickness of coating increases, and so does electric resistance in the coating. In order to maintain the constant voltage over the MAO process, the current density has to be reduced (shown in Fig. 1), which results in a reduction in the discharge energy of a single pulse. Consequently, with decreasing the discharge energy, the growth rate of coating decreases.

### 3.3. Microstructure characterization

Fig. 3 is the surface morphologies of the coatings prepared by MAO on NiTi alloy at different treatment times. It could be seen that the typical MAO porous structure is observed at different treatment times and the growth of the coatings is layer-by-layer

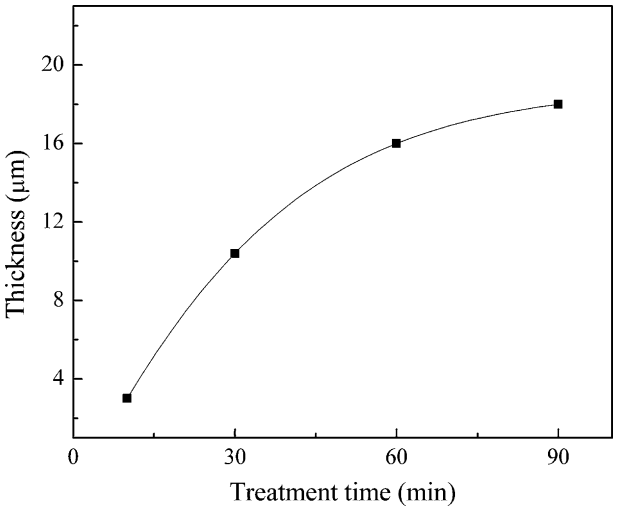


**Fig. 2.** The thickness of MAO coatings deposited on NiTi alloy at different treatment times.