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Characterization and corrosion behavior of hydroxyapatite/zirconia composite coating on NiTi fabricated by electrochemical deposition

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ABSTRACT

NiTi alloy is used as biomaterial due to its unique properties, but the high content of Ni (about 50 at.%) in biomedical NiTi is concerned. Hydroxyapatite and hydroxyapatite/zirconia composite coatings were directly electrodeposited on NiTi alloy surface. The coated samples were characterized using X-ray diffraction, scanning electron microscopy, infrared spectroscopy, bonding strength test, polarization and EIS. Results showed that when ZrO_2 was added into the electrolyte, morphology of HAP was changed from thin flake-flower-like crystals to needle-flower-like crystals, and coating was denser. Besides, HAP crystal grains in the coating were preferentially arranged in the [0 0 1] direction. Addition of ZrO_2 could improve the bonding strength between the coating and the substrate. Corrosion resistance of NiTi in the simulated body fluid at 37 °C was significantly improved by almost 60 times by electrodeposition of the hydroxyapatite/zirconia composite coating.

1. Introduction

Nickel–titanium (NiTi) shape memory alloy (SMA) is well known for its unique physical and mechanical properties, such as shape memory effect, good strength, and super-elasticity [1–4]. In recent years, NiTi alloy is used as biomaterial due to its unique properties well [5,6]. However, the high content of Ni (about 50 at.%) in biomedical NiTi SMA is of great health concern, which can trigger the risk of allergy and adverse reactions when its ions are released into the human body [7,8]. Therefore, it is necessary to improve the corrosion resistance of the NiTi alloy and suppress the release of Ni ions by surface modification technique.

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) has been available clinically for use in dentistry and medicine in recent years due to its excellent biocompatibility and osteoconduction [9]. The HAP coating can satisfy the dual properties. HAP is a major inorganic component of natural bone and can accelerate the bone growth [10,11]. But the mechanical strength of HA is too poor to be used in load-bearing applications. Therefore, HA coating was deposited on the surface of metallic implants to improve the biocompatibility property [12]. Zirconia (ZrO_2) is a ceramic and is bioinert, which shows good wear resistance, corrosion resistance and biocompatibility. Besides, it shows high strength and toughness index, therefore, adding ZrO_2 into HAP coating is an effective method to improve the interfacial bonding strength of the matrix and coating [13,14].

Until now, there are many researches about HAP coating on titanium and titanium alloy [15–18]. But corrosion behavior of hydroxyapatite coating or hydroxyapatite/zirconia composite coating on NiTi directly fabricated by electrochemical deposition is hardly reported. In this work, hydroxyapatite/zirconia composite coating on NiTi was directly prepared by electrodeposition, and corrosion behavior of hydroxyapatite/zirconia composite coating was studied by electrochemical corrosion test. The research proved that the coating evidently improved corrosion resistance and biocompatibility of NiTi and effectively prevented precipitation of Ni ions.

2. Material and methods

2.1. Samples preparation and electrodeposition

The substrate material used in this study was the NiTi (Ni, 55.84 wt.%) alloy. The specimen was cut into size of 10 mm × 10 mm × 2 mm. NiTi samples were mechanically polished successively with SiC papers of different grit 400, 800, 1000, 2000. These samples were then ultrasonically cleaned with acetone and deionized water for 10 min, respectively, and dried in air before electrochemical deposition.

The electrolyte solution contained 0.0167 M $Ca(NO_3)_2$, 0.01 M $NH_4H_2PO_4$, 0.1 M $NaNO_3$, 10 ml/L H_2O_2. $NaNO_3$ was added to improve the ionic strength of the electrolytes, and H_2O_2 was

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Table 1
Chemical composition of simulated body fluid (SBF).

Component	Concentration (g/L)
NaCl	6.6682
$NaHCO_3$	2.2682
KCl	0.2237
$K_2HPO_4{\cdot}3H_2O$	0.2283
$MgCl_2{\cdot}6H_2O$	0.3060
$CaCl_2$	0.2771
$NaSO_4$	0.0711

added to erase the evolution of H_2 gas and promote the deposition of dense coating. The pH of the electrolyte was adjusted to 6.0 at 25 °C by ammonia water and nitric acid. For the fabrication of HAP/ZrO_2 composite coatings, 7 g/L ZrO_2 (typical size about 40–50 nm, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) was added into the electrolyte. Electrodepositon was carried out in a cell consisting of NiTi as the anode, a graphite plate as the cathode. The deposition was carried out in galvanostatic mode and the current density was maintained at 0.5 mA/cm^2 for 40 min, keeping the temperature at 65 °C. Pure HAP coating was designated as control. The samples were washed with deionized water and dried at room temperature in air after deposition.

2.2. Surface microstructure characterization

The morphologies of samples were observed on a field-emission scanning electron microscopy (FE-SEM, JEOL-JSM-6700F) at 5.0 kV. Microstructural characterization in terms of the phases was analyzed by X-ray diffraction (XRD; Model D/max, Rigaku Co, Japan) with Cu K_α radiation (40 kV, 150 mA). The deposit powder scrapped from the titanium substrates was used in spectroscopic analysis carried out by FT-IR (AVATAR) using KBr pellet technique. The thickness of coatings was measured using a microprocessor coating thickness gauge (MiniTest 4100, Elektrophysik, Germany). The average thickness of the each of samples was obtained from 10 measurements at different positions.

2.3. Measurement of the bonding strength between the coating and the substrate

The interfacial bonding strength between the coating and the substrate was measured using an electronic universal testing machine (CSS-4410, China) at a crosshead speed of 5 mm/min. Coating bonding strength was determined by applying a uniaxial tensile load to a test assembly composed of a coated sample bonded to an uncoated substrate with epoxy adhesive. There were five parallel samples whose average value was used to calculate the bonding strength.

2.4. Electrochemical corrosion test

The electrochemical impedance spectroscopy (EIS) and polarization were performed by ZAHNER IM6 electrochemical workstation (Germany) at the temperature 37 °C in the simulated body fluid (SBF). The working cell was a standard three-electrode cell having a Pt net as counter electrode, saturated calomel electrode (SCE) as reference electrode and modified NiTi as working electrode. The surface area of sample was 1 cm^2, and the simulated body fluid was used as the electrolyte and an electrolyte temperature of 37 °C was applied. The SBF solution (composition given in Table 1) was prepared by dissolving reagent-grade mixtures of NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, and Na_2SO_4 in distilled water and buffering at pH 7.40 with tris-hydroxymethyl aminomethane and hydrochloric acid (HCl) at 37 °C. All measured potentials presented in this paper were referred to SCE. For EIS study, a small amplitude signal of 10 mV was applied to the samples over a frequency range of 0.01 Hz to 100 kHz recoding with 56 points. Polarization tests were carried out with a sweep rate of 20 mV/s, sweeping potential from −600 mV to 600 mV.

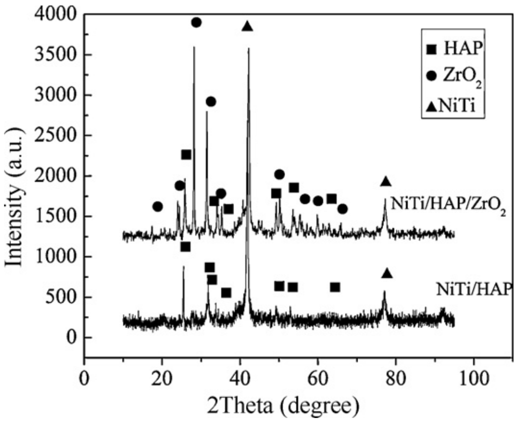

Fig. 1. XRD patterns of HAP coating and HAP/ZrO_2 coating.

3. Results and discussion

3.1. Coating characterization

Fig. 1 shows the XRD patterns of the coatings on NiTi alloy after electrochemical deposition. Taking no account of the substrate peaks, all XRD peaks from hydroxyapatite coating can be ascribed to apatite, which indicates that pure hydroxyapatite coating was fabricated by electrochemical deposition. And, the XRD pattern of hydroxyapatite/zirconia composite coating confirms that the deposits are the HAP and ZrO_2 crystals. The HAP peaks of the coatings show that the highest peak intensity is (0 0 2) crystal face instead of (2 1 1) crystal face, which means crystal grains in the coating were preferentially arranged in the [0 0 1] direction, i.e. *c*-axis [19].

The FT-IR spectra of the deposits obtained in the electrolytes are shown in Fig. 2. The spectra are almost the same, exhibiting typical character of the HAP crystals. The bands at 566, 602, 1032 cm^{-1} are the vibration absorption peaks of the phosphate ions. The bands at 3570 and 637 cm^{-1} correspond to the stretching and wagging vibrations of the OH group. 1636 cm^{-1} is the absorption peak of the adsorbed water; and 1421 cm^{-1} is the absorption peak of carbonate ion, owing to CO_2 in air absorbed by the electrolyte. It can also found the weak peak of carbonate ion shows the low content. By

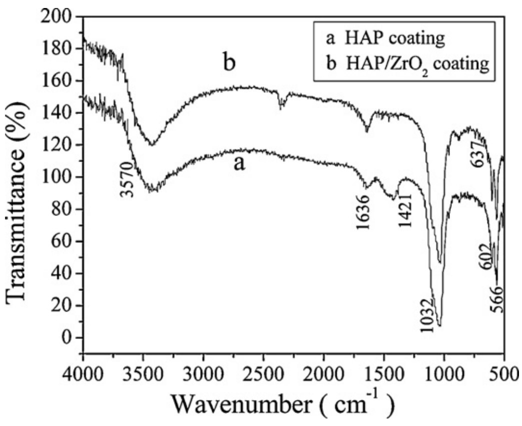

Fig. 2. FT-IR spectra of deposits scraped from NiTi substrates.