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Enhanced corrosion resistance and in vitro bioactivity of NiTi alloys modified with hydroxyapatite-containing Al_2O_3 coatings

Xiyuan Wang[a], Fu Liu[b,*], Ying Song[a,*]

[a] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, PR China
[b] School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China

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ABSTRACT

Hydroxyapatite (HA)-containing Al_2O_3 coatings were prepared on NiTi alloys through a cathodic plasma electrolytic deposition (CPED) process, followed by hydrothermal treatment (HT). The surface morphology, elemental distribution and phase composition of each coating were studied by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD). SEM observations revealed that the coatings exhibited a "crater-like" porous structure, and that the thickness of the coating could be up to 100 μm. The results of EDS demonstrated that the Ca and P concentrations in the Al_2O_3 coatings could be increased to 8.2% and 4.7%, respectively, and that the Ca/P ratio could reach 1.72, which was close to that of natural HA. The results of XRD analysis showed that the CPED coating mainly comprised α-Al_2O_3 and γ-Al_2O_3, and that HA crystallization was induced by the subsequent HT. The corrosion resistance of the samples was investigated by potentiodynamic polarization tests and electrochemical impedance spectroscopy (EIS). The results showed that the corrosion resistance of the sample with the CPED-HT coating was enhanced by more than two orders of magnitude compared to that of the uncoated NiTi alloy. Ni ion release in simulated body fluid (SBF) was characterized by inductively coupled plasma-atomic emission spectroscopy, and the results showed a significant drop in the concentration of released Ni ions from 18.0 μg/mL for the uncoated NiTi alloy to 0.7 μg/mL for the CPED-HT coating. In addition, the SBF soaking test showed that HA precipitated on the CPED-HT coating and that the HA layer became thicker and larger with increasing soaking time, indicating that the CPED-HT coating exhibited excellent apatite-inducing ability. Thus, the introduced CPED-HT treatment provides a new and effective route for the surface modification of NiTi alloys for use as biomedical materials.

1. Introduction

Recently, NiTi alloys have been receiving increasing interest as promising bone bonding implants due to their good shape memory effect (SME), high superelasticity, low stiffness and low Young's modulus [1,2]. However, their poor biocompatibility and bioactivity limit applications in load-bearing implants. For this reason, coatings of $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite [HA]), the main inorganic component of bones and teeth, have been used to improve the bioactivity of NiTi alloys; this would combine the superior mechanical performance of the metal component with the excellent biological responses of HA [3]. Several surface modification techniques have been developed to fabricate HA coatings on NiTi alloys, including electrochemical deposition [4], a sol-gel method [5], laser surface treatment [6] and chemical treatment [7], etc. In addition, micro-arc oxidation (MAO, also known as plasma electrolytic deposition [PED] or plasma electrolytic oxidation [PEO]) has been applied for the surface modification of NiTi alloys [8–10]. MAO-based modification has many advantages over other technologies, such as good corrosion resistance, high bonding strength, and high hardness.

Researchers have attempted to apply MAO with Ca- and P-containing electrolytes to the fabrication of HA-coatings on the surfaces of Ti, Ti-6Al-4 V, Mg and NiTi [11–13]. However, in most cases, HA could not be formed directly on the samples via one-step MAO treatments. A subsequent hydrothermal treatment (HT), however, may be applied to increase the crystallization of HA, which may effectively improve the bioactivity of the coating.

As a new kind of MAO technique, cathodic plasma electrolytic deposition (CPED), has been used for the surface modification of Ti, Mg and stainless steel. For example, Jin et al. [14] prepared Al_2O_3 coatings on titanium substrates by CPED method in an $Al(NO_3)_3$ ethanol solution. Karimi et al. [15] fabricated ZrO_2 coatings on 316L stainless steel by CPED technique in a potassium hexafluorozirconate (K_2ZrF_6) electrolyte solution. In Liu et al. [16], Al_2O_3-ZrO_2 ceramic coatings were

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* Corresponding authors.
E-mail addresses: fuliu@hit.edu.cn (F. Liu), songy@hit.edu.cn (Y. Song).

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prepared on WE43 Mg alloys by CPED technique in an electrolyte mixture of $Al(NO_3)_3$, $Zr(NO_3)_4$, and ethanol. However, few reports have reported the application of CPED to NiTi alloys. Recently, we prepared Al_2O_3 ceramic coatings on NiTi substrates using CPED [17], resulting in a reduction in the amount of Ni to less than the detection standard; concomitantly, the corrosion resistance had tripled, based on the corrosion current density after CPED. It is worth noting that the CPED technique depends largely on the composition of the available electrolytes, suggesting that it could be a promising technique to introduce particular ions, such as Ca and P, into the CPED-based coatings by adjusting the composition of the electrolyte solution.

In this study, HA-containing Al_2O_3 ceramic coatings were prepared on NiTi substrates using CPED combined with an HT (this kind of coating is called CPED-HT coating here). To our knowledge, this is the first report on triethyl phosphate (TEP) acting as the P source in the CPED process, which solves issues with the incorporation of P that are typically caused by the repulsion effects due to electrical charges. The structures and compositions of the CPED and CPED-HT coatings were systematically characterized by scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Meanwhile, the corrosion resistances of the NiTi alloys were evaluated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. The Ni ion concentrations and release rates were evaluated by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). In addition, the in vitro bioactivity of CPED-HT coatings was comprehensively characterized by simulated body fluid (SBF) soaking tests. This NiTi alloys modified with CPED-HT coatings are expected to be useful as advanced biomaterials for medical implantation due to their reduced Ni ion release, improved corrosion resistance, and good bioactivity.

2. Experimental details

2.1. Sample preparation and characterization

2.1.1. Specimen preparation and CPED process

Commercially available NiTi alloy (component: 49.2% Ti and 50.8% Ni) with square shape (sample size 15 mm × 15 mm × 1 mm) was used as substrate for the CPED process. All samples were polished by 320, 1000, and 2000 grits SiC paper, and then rinsed with acetone and distilled water in an ultrasonic cleaner for 10 min. The CPED electrolyte mixture comprised different amounts of $Ca(NO_3)_2{\cdot}4H_2O$ (acting as the Ca source), $C_6H_{15}O_4P$ (triethyl phosphate [TEP], acting as the P source), 0.2 M $Al(NO_3)_3{\cdot}9H_2O$ and ethanol. In order to adjust the Ca/P ratio to be close to the natural Ca/P ratio in HA of 1.67, the ratio of calcium nitrate and TEP was kept at 1:10. The used calcium nitrate concentrations were 0.01, 0.02, 0.03, and 0.04 M, while the TEP concentrations were 0.1, 0.2, 0.3, and 0.4 M, respectively. CPED was performed with a constant voltage of 450 V, supplied using bidirectional pulse power, with the NiTi samples functioning as the cathodes and the stainless steel containers as the anodes. The CPED treatment time was 45 min, the frequency was 100 Hz, and the duty cycle was 15%. The electrolyte temperature during CPED was controlled below 30 °C by stirring and cold water cooling. After CPED, the samples were rinsed with distilled water and air dried. Finally, the CPED coated NiTi plates were immersed in Teflon-lined autoclaves (volume: 50 mL) in 20 mL deionized water and hydrothermally treated at 240 °C for 2 h.

2.1.2. Surface characterization

SEM (S4800, Hitachi Co., Japan) was used to observe the surface morphology. Meanwhile, EDS (Oxford Model 7537, United Kingdom) was employed to study the composition of each CPED coating. The phase compositions of the CPED coatings were studied by XRD (D/max-2500, Rigaku Co., Japan) using Cu Kα radiation with continuous scanning at a rate of 5°/min; the accelerating voltage and current were set at 40 kV and 40 mA, respectively. XPS (PHI 5700, Physical Electronics, USA) using an Al Ka X-ray source (beam energy: 1486.6 eV) was used to investigate the chemical compositions and chemical valence states of the CPED coating elements. An eddy current-based surface roughness gauge (TR-100, Time Co., China) was used to measure the roughness of each sample; the Ra parameter was used for surface roughness characterization. Each sample roughness was tested for five times and the mean values were calculated. Finally, the thickness of each coating was measured using an eddy current-based surface thickness gauge (TT-260, Time Co., China).

2.2. Corrosion resistance and Ni ion releasing test

2.2.1. Electrochemical tests

EIS and potentiodynamic polarization tests were conducted to evaluate the corrosion resistance of both uncoated and CPED-coated NiTi samples. A conventional electrochemical cell with three electrodes was used with a saturated calomel electrode (SCE) and Pt foil as the reference and auxiliary electrodes, respectively. This test was performed at 37 °C in a Hank's solution (0.06 g/L $MgSO_4$, 0.4 g/L KCl, 0.06 g/L $Na_2HPO_4{\cdot}2H_2O$, 0.06 g/L KH_2PO_4, 1 g/L Glucose, 0.35 g/L $NaHCO_3$, 0.14 g/L $CaCl_2$, 0.1 g/L $MgCl_2{\cdot}6H_2O$ and 8 g/L NaCl; pH 7.4) using a CHI604D electrochemical analyzer (Chenhua, Shanghai, China). The samples were left with only one side of 1 cm^2 exposed to the Hank's solution, which served as the working electrode. Prior to the start of EIS, the samples were kept in the solution for 30 min to allow the open circuit potential to reach a quasi-steady state. The amplitude of sinusoidal perturbation was 10 mV, and the scan frequency ranged from 10 kHz to 0.01 Hz. Subsequently, EIS data were analyzed with ZSimpWin software (Version 3.30d, USA) and fitted to appropriate equivalent circuit (EC) models.

Following the EIS measurements, potentiodynamic polarization tests were carried out over the potential range from 0.25 V below to 0.25 V above the open circuit potential; the polarization scan rate was 0.167 mV/s in the anodic direction. Finally, the results, i.e., corrosion potential (E_{corr}) and corrosion current density (i_{corr}), were calculated by the special analysis mode of the CHI604D analyzer using the Tafel extrapolation method.

2.2.2. Ni ion release test

ICP-AES analyses were performed to evaluate the amount of Ni ions released into SBF and the Ni ion release rate. In order to investigate the Ni ions release rate, all samples, i.e., uncoated, CPED-treated and CPED-HT-treated NiTi substrates, were tightly sealed leaving exposed areas of 1 cm^2. Then, they were soaked in a polypropylene bottle containing 35 mL SBF solution for 7, 14, 28, 42, and 56 days at 37 °C. The Ni ion concentrations accumulated in the SBF solution after soaking were measured using an Agilent 5110 ICP-AES system (Hewlett-Packard, Yokogawa Analytical Systems, Tokyo, Japan). The wavelength of the spectrometric line corresponding to Ni was 233.7 nm.

2.3. Evaluation of bioactivity

In vitro SBF soaking tests were performed to study the bioactive behavior of the NiTi alloy treated by the CPED-HT technique. The SBF solution used in this research comprised several reagent grade chemicals with ion concentrations closely resembling those of human blood plasma [18], i.e., NaCl (7.996 g/L), $NaHCO_3$ (0.350 g/L), KCl (0.224 g/L), $K_2HPO_4{\cdot}3H_2O$ (0.228 g/L), $MgCl_2{\cdot}6H_2O$ (0.305 g/L), $CaCl_2$ (0.278 g/L), and Na_2SO_4 (0.071, g/L). The pH value of SBF was adjusted to 7.4 with 1 M HCl and $C4H_{11}NO_3$ (tris (hydroxymethyl) methyl aminomethane [THAM]) after all the above-mentioned chemicals were dissolved in distilled water.

In the following soaking process, samples were immersed in SBF solution for various periods (2, 7, or 14 days) at 37 °C in a plastic container containing 35 mL SBF. The SBF solution was exchanged every two days to avoid any changes in cationic concentration and minimize