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The effect of NaOH concentration on the steam-hydrothermally treated bioactive microarc oxidation coatings containing Ca, P, Si and Na on pure Ti surface

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ABSTRACT

The microarc oxidation (MAO) coating covered pure Ti plates are steam-hydrothermally treated in autoclaves containing NaOH solutions with different concentrations of 0, 0.001, 0.01, 0.1 and 1 mol·L^{-1}. Due to the composition of Ti, O, Ca, P, Si and Na elements in the MAO coating, anatase and hydroxyapatite (HA) crystals are generated from the previously amorphous MAO coating after the steam-hydrothermal treatment. Meanwhile, it is noticed that the amount of HA crystals increases but showing a decline trend in aspect ratio in morphologies with the increasing of NaOH concentration. Interestingly, the steam-hydrothermally treated MAO coatings exhibit better bonding strength with Ti substrate (up to 43.8 ± 1.1 MPa) than that of the untreated one (20.1 ± 3.1 MPa). In addition, benefiting from the corrosive attack of the dissolved NaOH in water vapor on the MAO coating, Ti–OH is also formed on the steam-hydrothermally treated MAO coating surface, which can trigger apatite nucleation. Thus, the steam-hydrothermally treated MAO coatings exhibit good apatite-inducing ability.

1. Introduction

Titanium (Ti) is widely applied in the production of hard tissue implants (such as bones, joints and teeth) on account of its excellent biocompatibility, high corrosion resistance and good osseointegration [1]. Despite reports of Ti implants indicate direct bonding to bone [2], the Ti implant surface does not form a chemical bond with bone tissue. For the last decade, various surface modifying techniques (including plasma spraying [3,4], sol–gel method [5,6], and electrochemical deposition [7–9]) have been investigated to fabricate bioactive films such as hydroxyapatite (HA) and bioactive glass-ceramic on Ti, which spontaneously bond to the living bone [10]. Among them, MAO coatings have gained much attention in recent years, since both the structure and elemental concentration of the MAO coating can be conveniently and effectively adjusted by changing the parameters [11,12].

Herein, a Ca, P, Si and Na incorporated MAO coating has been formed on pure Ti surface [13]. However, like most of the bioactive MAO coatings according to the previous researches [14–18], it shows a poor apatite-inducing ability. Therefore, subsequent modifications, including hydrothermal treatment [19–23], have been used to modify the MAO coating via forming Ti–OH and HA on the surface, which is beneficial to the induction of apatite. Unfortunately, reports [21,22] also suggest that the incorporated elemental concentration and mechanical properties of the MAO coating are cut by the hydrothermal treatment. Once the MAO coating covered Ti plates are immersed into the hydrothermal solutions, the incorporated elements in the coating fast migrate and dissolve into the solutions during the treatment [24]. Meanwhile, the as-formed titanate hydrate film directly reduces the adhesive strength between the coating and the Ti substrate [25–27]. By this way, the cell adhesion and bone integration properties are also limited after implantation.

To combine the benefits of the as-formed HA and Ti–OH, and avoid the drawbacks of the decline in incorporated elemental concentration and mechanical properties, a restively new technology, steam-hydrothermal treatment, via using vapor to react with the MAO coating is performed in this work. During the treatment, the MAO coating covered pure Ti plates are hanged in the autoclave with Teflon-lined fixture without touching the solution (Fig. 1), and the temperature is set at 200 °C for 24 h. Furthermore, as the corrosive attack of OH groups on the MAO coating is the key factor for the formation of HA and Ti–OH [21, 27], NaOH solutions with different concentrations of 0, 0.001, 0.01, 0.1 and 1 mol·L^{-1} are used in the treatment to enhance the apatite-inducing ability. Because there is no report about the effects of NaOH

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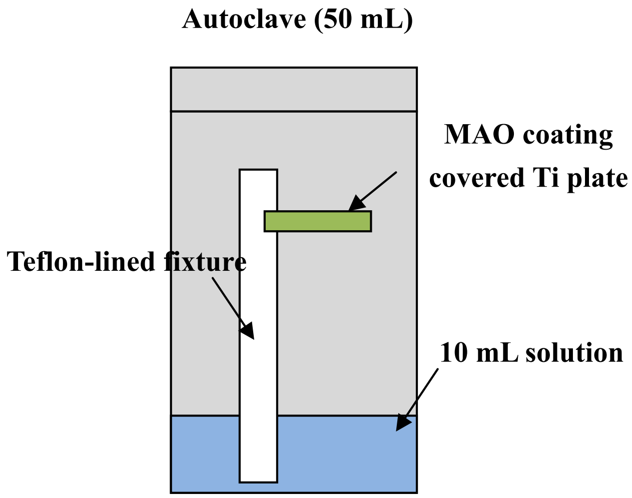

Fig. 1. Schematic diagram for the steam-hydrothermally treatment.

concentrations on the steam-hydrothermal treated MAO coating on pure Ti plate, its influences on the microstructures, phase composition, mechanical properties and apatite-inducing ability of the steam-hydrothermally treated MAO coatings are discussed thoroughly in this work.

2. Materials and methods

2.1. Microarc oxidation

In the MAO process, pure Ti plates ($10 \times 10 \times 1$ mm^3) were used as anodes, and stainless steel plates were used as cathodes in an electrolytic bath. The pure Ti plates were ground with abrasive papers, ultrasonically washed with acetone and distilled water, and dried at 40 °C. The electrolyte was prepared by dissolving of $Ca(CH_3COO)_2 \cdot H_2O$ (8.8 g·L^{-1}), Na_2SiO_3 (7.1 g·L^{-1}), $Ca(H_2PO_4)_2 \cdot H_2O$ (6.3 g·L^{-1}), EDTA-2Na (15 g·L^{-1}) and NaOH (5 g·L^{-1}) in deionized water. The applied voltage, pulse frequency, duty cycle and oxidizing time were set at 350 V, 600 Hz, 8.0% and 5 min, respectively. In this way, the MAO coating containing Ca, P, Si and Na was prepared on pure Ti plate surface.

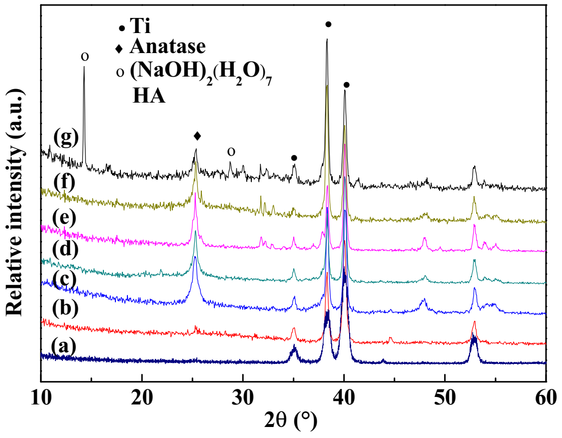

Fig. 2. XRD patterns of pure Ti plate and the MAO coating covered ones before and after steam-hydrothermally treating with NaOH solutions at different concentrations: (a) pure Ti plate, (b) MAO coating covered pure Ti plate, (c) SHT-0, (d) SHT-0.001, (e) SHT-0.01, (f) SHT-0.1 and (g) SHT-1.

2.2. Steam-hydrothermal treatment

The MAO coating covered pure Ti plates were hanged up in the Teflon-lined autoclaves with Teflon-lined fixture (Fig. 1). Only 10 mL NaOH solutions with different concentrations of 0, 0.001, 0.01, 0.1 and 1 mol·L^{-1} were added into the autoclaves with the volume of 50 mL. The reason for this is to ensure that the hanged samples are not touched or immersed in the solution. Then, the autoclaves were kept at 200 °C for 24 h. After the steam-hydrothermal treatment, the prepared pure Ti plates were collected and directly dried at 40 °C. In the following, the SHT-0, SHT-0.001, SHT-0.01, SHT-0.1 and SHT-1 were used to represent the steam-hydrothermally treated MAO coating on pure Ti plate, corresponding to various NaOH concentrations, respectively.

2.3. Simulated body fluid immersion

Pure Ti plate and the MAO coating covered pure Ti plate, as well as the steam-hydrothermal treated ones were soaked in 15 mL simulated body fluid (SBF) [28] for different times of 7 and 14 days to evaluate their apatite-inducing ability. And the SBF was refreshed every other day. The SBF was prepared by dissolving NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, and Na_2SO_4 into deionized water. At last, it was buffered at pH 7.40 with tris-hydroxymethylaminomethane ($(CH_2OH)_3CNH_2$) and 1.0 mol·L^{-1} HCl at 37 °C.

2.4. Structure characterization

2.4.1. X-ray diffraction (XRD)

Before and after immersion in the SBF, the phase composition of the plate samples was analyzed by X-ray diffraction (XRD, D/max-γB, Japan) using a CuKα radiation with a continuous scanning mode at a rate of 4°·min^{-1}. The accelerating voltage and current were set at 40 kV and 50 mA.

2.4.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDS)

Scanning electron microscopy (SEM, Helios Nanolab 600i, FEI Co., USA) was used to observe the surface and cross-sectional morphology. In addition, the elemental concentrations of the samples were detected by an energy dispersive X-ray spectrometer (EDS, EDAX, USA) equipped on the SEM system.

2.4.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FT-IR, Magna-IR 560 E.S.P., USA) was used to analyze the sample surface. In the preparation, the powders were collected by blade scratching from the surface layer of the samples. Approximately 1 mg of the collected powder mixed with about 500 mg of dry KBr powder was ground using an agate mortar and pestle. The mixed powder was pressed into transparent disk with a diameter of 13 mm for the FT-IR work. In the FT-IR experiment, the scanning range and resolution were 4000–400 and 4 cm^{-1}, respectively. Additionally, at least 5 samples of the SHT-0.1 were used to collect enough powder by blade scratching, because the surface of SHT-0.1 was very hard.

2.4.4. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM, TecnaiG2F30, FEI Co., USA) with an accelerated voltage of 300 kV was used to analyze the microstructure of the nanowire formed on the SHT-0.1. In the TEM operation, the morphology of the nanowire was observed. And high resolution of TEM (HRTEM) pattern was analyzed by fast Fourier transform (FFT) and inverse fast Fourier transform (IFFT) techniques to identify its phase. The elemental composition was analyzed by EDS equipped on the TEM system.