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Hydrothermal calcification of bioglass film in $CaHPO_4$ solutions

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ABSTRACT

Bioglass film was sol-gel coated on titanium substrate, followed by hydrothermal treatment in water, 2.5 mM and 10 mM $CaHPO_4$ solutions, respectively. X-ray diffraction analysis reveals amorphous nature of the gel powder sintered at 610 °C, but small diffraction peaks of Ca_3SiO_5 are also observed. The absorption bands of Si-O-Si bonds, PO_4 and OH groups are present, while those of NO_3 groups are absent in Fourier transform infrared spectrum of the sintered gel powder. Scanning electron microscopy observation shows that the surface of the sintered bioglass film is porous (pore size ~200 nm), and nanocrystallites (width ~20 nm, length ~200 nm) are deposited on the samples hydrothermally treated in $CaHPO_4$ solutions. Energy dispersive x-ray, x-ray photoelectron spectroscopy and x-ray diffraction analyses indicate that the nanocrystallites are composed of hydroxyapatite, which are formed through a dissolution-precipitation reaction. The formation of hydroxyapatite nanocrystallites at the film surface improves hydrophilicity of the coating samples. Potentiodynamic polarization test in the Ca-free Hank's solution demonstrates that the coating samples have better corrosion resistance than the polished one. The calcified titanium samples are expected to possess good biological properties.

1. Introduction

Bioglass is a kind of bioactive material, and it has recently been used to improve bioactivity and corrosion resistance of biomedical metals [1–4]. Sol-gel coating is a good method to prepare bioglass and other ceramic or hybrid films, with the advantages of the independence of substrate shape, good control of coating composition, the relative ease of processing, etc.

In order to enhance bioactivity and chemical stability of bioglass, hydroxyapatite (HA) and forsterite were added into, and HA or mesoporous silica films were deposited onto bioglass and its coatings [5–7]. Moreover, HA nano-rods were hydrothermally prepared on bioglass film in the simulated body fluid, to mimic the needle-like morphology of bone apatite crystallites [8]. During the hydrothermal treatment, the elongated HA nano-rods deposited on the surface via a dissolution-precipitation reaction. It is known that $CaHPO_4$ is slightly soluble in water (solubility 4.3×10^{-5} g/mL at 20 °C), and $CaHPO_4 \cdot 2H_2O$ has been proposed as an intermediate in bone mineralization [9]. In our previous work [10], $CaHPO_4$ solution was used for hydrothermal calcification of Ti6Al4V alloy, with HA and TiO_2 nanocrystallites formed at the substrate surface. The $CaHPO_4$ solutions may provide a simple medium for hydrothermal growth of HA nanocrystallites on bioglass films.

In this work $CaHPO_4$ solutions are used for hydrothermal calcification of sol-gel prepared bioglass film on titanium substrate. Microstructure, chemical composition, hydrophilicity and corrosion resistance of the coated titanium samples are investigated.

2. Experiment

The bioglass sol was prepared by the following method [8]. Briefly, 1.40 g calcium nitrate, 6.20 mL tetraethyl orthosilicate, 350 μL triethyl phosphate and 29 mL ethanol were mixed, followed by addition of 500 μL nitric acid solution (1 mol/L) as catalytic hydrolysis. The molar ratio of Si: Ca: P was 78: 16: 6. The mixture was stirred at 40 °C for 4 h and aged overnight at room temperature.

Titanium plates (size $10 \times 10 \times 1.2$ mm) were polished with abrasive papers down to grits 1200, ultrasonically cleaned in acetone, ethanol, deionized water in sequence, and dried in air. The plates were dipped in the above sol and withdrawn at a speed of 30 mm/min with a dip coater. The sample was heat treated at 350 °C for 10 min in an electric furnace, with the ramping rate of 5 °C/min. The dip coating was repeated, and the sample was heat treated at 610 °C for 10 min (ramping rate: 5 °C/min before 350 °C, 10 °C/min after 350 °C) and allowed to cool down in the furnace. The bioglass coating samples were denoted as BG samples.

The BG samples were then subjected to hydrothermal treatment in deionized water, 2.5 mM and 10 mM $CaHPO_4$ solutions, respectively. The water/solution was put into a Teflon-lined autoclave (25 mL) with the filling ratio of ~80%. The sample stood vertically in the autoclave with the help of a Teflon clamp. The autoclave was sealed and heated at 120 °C for 14 h. After the treatment, the samples were evacuated,

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rinsed with deionized water for several times and dried. The samples treated in water, 2.5 mM and 10 mM $CaHPO_4$ solutions were denoted as HS-A, HS-B and HS-C, respectively. The samples prepared by directly putting the dip coated samples in a hot furnace for sintering (400 °C, 10 min) were also hydrothermally treated in the above media for control study. In addition, the sol was dried at 80 °C for several hours and the dried gel was sintered with the same heating route as that for BG samples.

Surface morphology of the samples was observed by scanning electron microscopy (SEM, FEI Quanta 600F) equipped with energy dispersive x-ray analysis (EDX). Elemental composition and chemical bonding state of the samples were examined by x-ray photoelectron spectroscopy (XPS, AlK_α, K-Alpha, VG). Phase structure of the coating and gel powder samples was analyzed by x-ray diffraction (XRD, CuK_α, X'Pert PRO). Component of the gel powder was analyzed by Fourier transform infrared (FT-IR) spectroscopy (Vertex 70, Bruker) with the KBr pellet technique.

Contact angle of the coating samples was measured with a contact angle goniometer under ambient conditions. Corrosion resistance of the samples was evaluated by potentiodynamic polarization test with an electrochemical workstation (CS150, Corrtest®) at ambient conditions. The electrolyte was the Ca-free Hank's balanced salt solution (HBSS, NaCl 8.00 g/L, KCl 0.40 g/L, $NaHCO_3$ 0.34 g/L, KH_2PO_4 0.06 g/L, $Na_2HPO_4 \cdot 12H_2O$ 0.12 g/L). A platinum electrode was used as counter electrode, and the saturated calomel electrode (SCE) was reference electrode.

3. Results and discussion

3.1. XRD and IR analyses of the sintered gel powder

The dried gel was sintered for XRD and FT-IR analyses (Fig. 1). The sintered gel powder is still amorphous, but small peaks of Ca_3SiO_5 (ICDD # 16–0406) are present in the XRD θ–2θ pattern. This observation agrees with the report that crystallized calcium silicate and sodium calcium silicate phases were detected in the sintered Si-Ca-P and Si-Ca-P-Na bioglasses, respectively [1,4]. In the FT-IR spectrum, the three absorption bands positioned at 1090, 803 and 466 cm^{-1} are attributed to the vibrations of Si-O-Si bonds. The small vibrational band located at 573 cm^{-1} is ascribed to PO_4 groups. The wide band centered at 3440 cm^{-1} is from OH groups in the gel. The absorption bands of NO_3 groups (around 1380 and 850 cm^{-1}) are absent, indicating the complete decomposition of calcium nitrate by the sintering at 610 °C [11,12].

3.2. SEM-EDX, XPS and XRD analyses of the coating samples

SEM images of the coating samples are shown in Fig. 2. The surface of sample BG is crack-free and porous, with the pore size about 200 nm. Larger pores are observed in Fig. 3(a) for the film that was prepared by directly putting the dip coated sample in a hot furnace for sintering (400 °C, 10 min). The pores originated from vaporization of water and organic molecules during the sintering treatment. For the hydrothermally treated sample HS-A, dissolution of the glass film is observed, and there are some nanoparticles at the surface. Nanocrystallites cover the surfaces of samples HS-B and HS-C, with the width of ~20 nm and the length of ~200 nm. In the EDX spectra (Fig. 4) sample HS-C has higher Ca and P peaks and lower Si peak compared with sample BG.

Chemical composition of the surface layer of sample HS-C was examined by XPS analysis, with the Ca 2p, P 2p, Si 2p and O 1s spectra shown in Fig. 5. The Ca 2p peaks (350.9 eV, 347.4 eV) and P 2p peak (133.4 eV) confirm calcium phosphate formed at the sample surface [13]. In the O 1 s spectrum, the sub-peak located at 529.6 eV can be assigned to TiO_2 [14]. The sub-peak at 531.0 eV accompanied by the P 2p peak at 133.4 eV is diagnostic of HA, rather than $CaHPO_4 \cdot 2H_2O$ [13]. The formation of HA is consistent with the report that HA nanorods were hydrothermally grown on bioglass film in the simulated body fluid at 120 °C [8]. The third sub-peak positioned at even higher binding energy is attributed to hydroxyl groups at the sample surface. The weak Si 2p peak indicates low content of Si in the surface layer.

XRD θ–2θ patterns of the coating samples are shown in Fig. 6. The diffraction peaks of titanium substrate and rutile TiO_2 are present for all samples. For the sample BG, the diffraction peak of glass film is not obvious due to the small film thickness. The diffraction pattern of sample HS-A is similar to that of sample BG, but diffraction peaks of HA are observed for samples HS-B and HS-C. Thus, $CaHPO_4$ solutions are favorable for the hydrothermal growth of HA at the bioglass film surface.

The nanocrystallites in Fig. 2c,d are composed of HA according to the above analyses. In order to study the growth mechanism of HA nanocrystallites, the coating samples sintered at 400 °C were also hydrothermally treated (Fig. 4b-d). Since the glass film was not crystallized due to the low sintering temperature, the dissolution of glass film was serious during the hydrothermal treatment in water, and thus the growth of HA is impeded. HA nanocrystallites are observed only for the sample that was treated in 10 mM $CaHPO_4$ solution. Therefore, HA nanocrystallites were formed at the glass film surface generally through a dissolution-precipitation reaction [8,15]. During the hydrothermal treatment, the hydrated silica produced by corrosion of bioglass provided favorable sites for apatite nucleation, and then Ca^{2+} and PO_4^{3-} ions in the solution would precipitate on the glass surface to form HA small crystallites.

3.3. Hydrophilicity and corrosion tests of the coating samples

Water contact angles of samples BG and HS-A are about 70° and 80°, respectively, while they are reduced to 23–30° for samples HS-B and

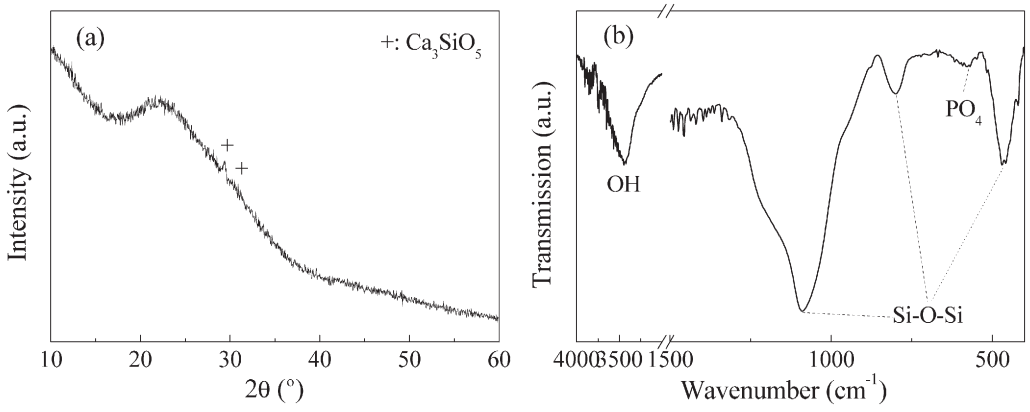

Fig. 1. (a) XRD θ–2θ pattern and (b) FT-IR spectrum of the sintered gel powder.