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In vitro apatite formation and visible-light photocatalytic activity of Ti metal subjected to chemical and thermal treatments

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Received 31 March 2014; received in revised form 18 April 2014; accepted 19 April 2014

Abstract

In this study, we investigated the surface structure, apatite formation in simulated body fluid (SBF), and visible-light photocatalytic activity of Ti metal subjected to chemical and thermal treatments. Ti metal samples treated with NaOH, a nitrogen-containing solution (0.1 M HNO_3, 0.1–1.0 M $(H_2N)_2C{=}O$, or 0.1–1.0 M NH_4Cl), and heat showed apatite formation on their surfaces in SBF, whereas those treated with NaOH, 0.5 or 1.0 M HNO_3, and heat did not. In the former case, apatite formation may be attributable to the fine network structure of anatase-type TiO_2 doped with a small amount of nitrogen on the surface of the Ti metal. The Ti metal treated with the latter treatment showed higher methylene blue decomposition than the untreated sample and the one treated with the former treatment. This preliminary result suggests that Ti metal treated with NaOH, 0.1 M HNO_3, and heat can potentially show visible-light-induced antibacterial property as well as bone-bonding ability.

Keywords: D. Apatite; Titanium metal; Visible-light photocatalytic activity; Simulated body fluid

1. Introduction

Titanium and its alloys have been widely used as artificial implants. In recent times, however, surgical site infection (SSI) has emerged as a serious problem that urgently needs a solution. To reduce the risk of SSI, many attempts have been made to develop antibacterial metallic medical devices [1–4]. We have focused on the antibacterial activity of N-doped TiO_2 under visible light [5] and tried to form this type of TiO_2 on Ti metal by surface chemical treatment. It has been reported that an anatase-type TiO_2 layer was formed on Ti metal when Ti metal was subjected to sodium hydroxide (NaOH), hot water, and heat treatment; the treated Ti metal showed apatite formation on its surface in simulated body fluid (SBF) [6]. Furthermore, Ti metal treated in this manner bonded to living bone through this apatite layer [7]. Based on these studies, we expect that novel Ti metal with visible-light-induced antibacterial property as well as bone-bonding ability might be obtained if N-doped TiO_2 is successfully formed on Ti metal by some surface chemical treatments.

Recently, we reported that a TiO_2 layer doped with a small amount of nitrogen (~0.16 at%) was formed on Ti metal by NaOH, ammonia (NH_4OH), and heat treatments and this treated Ti metal showed apatite-forming ability in SBF as well as methylene blue (MB) decomposition by visible light irradiation [8]. We also reported that Ti metal subjected to NaOH, nitric acid (HNO_3), and heat treatments showed no apatite formation in SBF although a larger amount of nitrogen (~1.1 at%) was doped on the Ti surface than in the earlier case. The loss of apatite-forming ability of the Ti metal subjected to NaOH, HNO_3, and heat treatments might be attributed to the dissolution of the surface $Na_{2-x}H_xTi_3O_7$ layer by acidic 1 M HNO_3 treatment [8,9]. Therefore, if we use a lower concentration of HNO_3 or another mild acidic or neutral nitrogen-containing solution, Ti metal with a higher amount of

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http://dx.doi.org/10.1016/j.ceramint.2014.04.109
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Please cite this article as: M. Kawashita, et al., In vitro apatite formation and visible-light photocatalytic activity of Ti metal subjected to chemical and thermal treatments, Ceramics International (2014), http://dx.doi.org/10.1016/j.ceramint.2014.04.109

doped nitrogen as well as apatite-forming ability in SBF might be obtained.

In this study, we attempted to form N-doped TiO_2 on Ti metal by NaOH, various concentrations of HNO_3, and heat treatments and investigated the apatite-forming ability of the samples in SBF and visible-light photocatalytic activity by examining MB decomposition. We also used a neutral urea ($(H_2N)_2C{=}O$) and mild acidic ammonium chloride (NH_4Cl) solution instead of HNO_3 as the nitrogen source.

2. Experimental procedure

2.1. Sample preparation

Commercially available pure Ti plates (10 mm × 10 mm × 1 mm; purity: 99.9%; Kojundo Chemical Laboratory, Japan) were used. They were abraded using no. 400 abrasive diamond paper and then washed with pure acetone and ultrapure water in an ultrasonic cleaner. The Ti plates were soaked in 5 mL of 5 M NaOH solution at 60 °C. The samples were subsequently soaked in 7 mL of either 0.1–1 M HNO_3, urea, or NH_4Cl at 40 °C for 24 h and were then gently washed with ultrapure water and dried. Special grade NaOH, HNO_3, $(H_2N)_2C{=}O$, and NH_4Cl were used in this study. All of these chemicals were purchased from Wako Pure Chemical Industries, Japan. The samples were heated to 600 °C at a rate of 5 $°C\ min^{-1}$ in an electric furnace (FO-100, Yamato Scientific, Japan), maintained at this temperature for 1 h, and then naturally cooled in the furnace to room temperature. Table 1 lists the abbreviated names of the samples subjected to various treatments.

2.2. Immersion of samples in SBF

The samples were soaked in 30 mL of SBF [10,11] containing ion concentrations (Na^+: 142.0 mM; K^+: 5.0 mM; Ca^{2+}: 2.5 mM; Mg^{2+}: 1.5 mM; Cl^-: 147.8 mM; HCO_3^-: 4.2 mM; HPO_4^{2-}: 1.0 mM; SO_4^{2-}: 0.5 mM) that were nearly identical to those in human blood plasma at 36.5 °C according to the ISO 23317: 2012 standard. After the samples had been immersed in SBF for 7 days, they were removed and gently washed with ultrapure water.

Table 1
Crystalline phases and Na and N contents on surfaces of samples subjected to various surface treatments.

Reagents	Concentration of reagent (M)	Crystalline phase	Na content (at%)	N content (at%)
HNO_3	0.1	Ti, rutile, anatase	0.28	0.73
	0.5	Ti, rutile	0.11	0.87
	1.0	Ti, rutile	0.13	1.63
$(NH_2)_2C{=}O$	0.1	Ti, anatase	5.7	0.22
	0.5	Ti, anatase	2.36	0.22
	1.0	Ti, anatase	1.21	0.21
NH_4Cl	0.1	Ti, anatase	0.35	0.23
	0.5	Ti, anatase	0.17	0.22
	1.0	Ti, anatase	0.64	0.21

2.3. Characterization of sample surfaces

The surface structures of the samples were investigated using a thin-film X-ray diffractometer (TF-XRD; RINT-2200VL, Rigaku, Japan; X-ray source: Ni-filtered Cu Kα radiation; X-ray power: 40 kV, 40 mA; scanning rate: 2 ° min^{-1}; sampling angle: 0.02°), scanning electron microscope (SEM; VE-8800, Keyence, Japan), and X-ray photoelectron spectrometer (XPS; AXIS Ultra DLD, Kratos Analytical, UK; X-ray source: monochromatic Al Kα radiation (1486.7 eV); X-ray power: 15 kV, 10 mA). Furthermore, in XPS, the binding energy was calibrated using the C_{1s} photoelectron peak at 284.8 eV as a reference. XPS peak analysis was performed using CasaXPS Version 2.3.15 software with all spectra Shirley background subtracted prior to fitting. The elemental composition was calculated from XPS spectra using the specific relative sensitivity factors for the Kratos Axis Ultra (O_{1s}: 0.78, Ti_{2p}: 2.001, N_{1s}: 0.477, C_{1s}: 0.278).

2.4. Evaluation of visible-light photocatalytic activity

The visible-light photocatalytic activity of the samples was evaluated by examining MB decomposition (Waldeck, Germany). The samples were soaked in 5 mL of 0.01 mM MB aqueous solution and incubated for 24 h to reach adsorption equilibrium. The MB aqueous solution was then replenished, and the samples were irradiated using two fluorescent lights (FL20SSEX-N/18X, NEC, Japan and FL20SS · N/18, Panasonic, Japan) for 6 h through an ultraviolet cutting filter (HGS05S, Lintec Commerce, Japan). The resultant cut-off wavelength was 350 nm and the distance between the sample and the filter was ~6 cm. The incident radiant flux density was fixed at 30 W/m^2. The MB concentration in the irradiated samples was examined using an ultraviolet visible (UV–VIS) spectrophotometer (PD-303, Apel, Japan) by measuring the UV absorbance at 664 nm. The MB concentration was also measured in unsoaked samples as a control. Three samples for each treatment condition were subjected to the above evaluation. The decrease in MB concentration (%) was calculated based on the difference in the MB concentration in the soaked and unsoaked samples, C_{sample} and C_{blank}, as follows [12]:

$$\text{Decrease in concentration (\%)} = (C_{blank} - C_{sample}) \times 100 / C_{blank} \tag{1}$$

3. Results and discussion

3.1. Surface structure of samples

Fig. 1 shows SEM photographs of the samples subjected to different treatments. A fine network structure that was typically formed on the sample after NaOH and heat treatments [13] was partially observed for the sample treated in 0.1 M HNO_3, whereas the samples treated in 0.5 and 1.0 M HNO_3 showed flat surfaces as did the untreated sample. In samples treated in $(NH_2)_2C{=}O$ and NH_4Cl, the fine network structure almost remained irrespective of the concentrations.

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