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Fabrication and characterization of oxygen-diffused titanium for biomedical applications

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Abstract

Although titanium has been successful as an orthopedic or dental implant material, performance problems still persist concerning implant–bone interfacial bonding strength. In this study a novel oxygen-diffused titanium (ODTi), fabricated by introducing oxygen into the titanium crystal lattice by thermal treatment, was investigated. The fabricated material is the result of a surface modification made on commercially pure titanium (cp Ti) previously coated with poly(vinyl alcohol) (PVA) by means of a thermal treatment performed at 700 °C in an ultra-pure argon atmosphere. The thermal treatment at 700 °C led to the formation of an anatase TiO_2 film on the cp Ti surface and a concentration gradient of oxygen into titanium. The surface of the fabricated ODTi consisted of an outer nanometric layer of anatase TiO_2 and an inner nanometric layer of Ti_2O_x ($x < 1$) in which the oxygen is in solid solution with the titanium metal. It was found that ODTi possesses in vitro apatite formation ability after being soaked into simulated body fluid (SBF) solution. This apatite formation ability is attributed to the presence of the anatase TiO_2 outermost surface layer and to abundant hydroxyl groups (–OH) formed on the ODTi surface after immersion in SBF.

Keywords: Oxygen-diffused titanium; Anatase TiO_2; Thermal oxidation; Simulated body fluid; Bioactivity

1. Introduction

Titanium implants have been widely used clinically for various types of bone-anchored reconstruction. A thin native oxide film that forms spontaneously on the titanium surface makes contact with the bone tissue and has been considered to be of great importance for successful osseointegration. However, insufficient bone–implant contact and fibrous encapsulation can cause the failure of dental implants [1]. Moreover, it has been reported that under in vivo conditions the stability of the passive layer could be altered [2]. Furthermore, analyses of retrieved implants have shown dissolution of metal ions on tissues adjacent to the implant [2].

Extensive efforts have been made to improve the bone bonding ability of titanium and to impart the desired surface properties by a modification of the naturally occurring passive film. Surface modification methods such as chemical (acid and alkali) treatment [3,4], electrochemical treatment (anodic oxidation) [5], sol–gel formation [6], chemical vapor deposition (CVD) [7], physical vapor deposition (PVD) [8], plasma spray deposition [9], ion implantation [10], thermal oxidation [11] have been employed to improve the quantity and quality of bone bonding and to develop a multifunctional implant surface by changing the composition, thickness, porosity, crystallinity and surface morphology of the native passive layer.

One of the simplest methods to generate an additional surface barrier layer on titanium is to treat it thermally in a furnace atmosphere, which produces a surface oxide layer. Thermal oxidation can generate thick and highly crystalline oxide films (principally based on rutile TiO_2),

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which is accompanied by the dissolution of oxygen beneath them. Depending on the oxidation regimes, gas atmospheres and heat treatment temperatures, either one monolayer of only TiO_2 or new oxide phases such as TiO_x ($x < 2$) can be formed on the titanium surface. However, much experimental work is needed to determine the proper conditions for the formation of a certain type of crystalline structure oxide(s) on titanium biomaterials in order to avoid spallation of the oxide layer from the substrate [12].

Several studies have provided evidence that thermal oxidation improves the hardness and the wear resistance of titanium [13–16], as well as the corrosion resistance [17–19]. On the other hand, according to Wang et al. [20,21] and Feng et al. [22] thermal oxidation is able to endow titanium with in vitro bioactivity since heat treatment at high temperatures increases the percentage of hydroxyl groups (OH^-) on the titanium surface, promoting the nucleation of bone-like apatite after immersion in simulated body fluid (SBF) [22]. Thermal oxidation has also been used to improve the bone response and the efficacy of dental implants in vivo. Two independent studies have demonstrated that thermal oxidation at 800 °C for 2 h in a pure oxygen atmosphere leads to enhanced bone formation around dental implants after functional loading [23,24]. However, they do not provide information on the role of the surface chemistry (and the resultant topography) on the enhanced osseo-integration of implants.

The thermal oxides produced at high temperatures strongly depend on the heat treatment conditions. Choi et al. [25] studied the oxides formed on titanium metal between 300 and 500 °C in air. They found the presence of only one oxide, rutile TiO_2. In general, the thermal oxidation of titanium in air or water vapor produces a thick, highly crystalline, rutile TiO_2 film. In the present work suitable conditions for growing anatase TiO_2 on a titanium surface by thermal oxidation were found. A compositional change in the native TiO_2 layer was achieved in a controlled inert atmosphere using a PVA-coated commercially pure titanium sample. The resulting material was named oxygen-diffused titanium (ODTi) and is interesting because it possesses a composite nanometric oxide film consisting of an anatase TiO_2 layer and oxygen interstitially inserted in the hcp Ti lattice (oxygen-diffused layer). Moreover, the material exhibits a capacity to bind OH^- groups on its surface after being immersed in water. The aim of the present work was to establish the optimum fabrication conditions of the ODTi in order to form an apatite layer on its surface in the presence of acellular SBF.

2. Materials and methods

2.1. Preparation of specimens

Titanium samples of 10 mm diameter were cut from commercially pure (cp) titanium sheet (Nilaco Co., Tokyo, Japan) of 0.5 mm thickness. After ultrasonic cleaning the samples in ethyl alcohol and distilled water, they were dip-coated into a 20 wt.% solution of poly(vinyl alcohol) (PVA) (Kanto Chemical Co., Tokyo, Japan). The degree of polymerization and saponification of the PVA polymer were 2000 and 72–82 mol%, respectively. The PVA was dissolved in distilled water by stirring the solution at 80 °C to ensure a homogeneous dispersion. The PVA-coated titanium substrates were allowed to dry on a glass plate at 70 °C overnight. During this process the solvent evaporates, leading to the formation of a hard PVA film on the titanium substrates. The specimens were moved to an alumina boat and placed inside an electric furnace to be thermally treated at several temperatures between 500 and 800 °C for 1 h in a high purity argon (99.999%) atmosphere. The exact gas composition was: $O_2 < 0.2$ ppm, $N_2 < 5$ ppm, $H_2 < 1$ ppm, $CO_2 < 1$ ppm, total hydrocarbons < 1 ppm, $H_2O < 1$ ppm. The argon flow rate was 50 $cm^3\ min^{-1}$. Before the thermal treatment the furnace was filled with argon at a flow rate of 100 $cm^3\ min^{-1}$ for 90 min. The samples were cooled inside the furnace to room temperature within about 6 h. Finally, the samples were sterilized in an autoclave at 121 °C for 15 min.

2.2. Surface characterization

The surfaces of the ODTi samples were observed by field emission scanning electron microscopy (FE-SEM) (Hitachi S-4500, Japan). An energy dispersive X-ray spectrometer (Horiba EMAX-7000, Japan) installed on the electron microscope was used to examine the elemental composition of the samples at an acceleration voltage of 20 kV. The effects of the thermal treatments on the crystalline structure were analyzed by X-ray diffraction (XRD) (Rigaku RAD-C system Tokyo, Japan) using Cu K_α radiation at 40 kV and 20 mA power. Data were recorded over the range $\theta = 20$–60°, with a step size of 0.02° and step duration of 0.4 s. At least four replicates were prepared for each sample. Phases found in the XRD patterns were identified by comparison with the standard JCPDS files. Modifications made on the surface of the oxygen-diffused titanium were monitored using a Fourier transform infrared (FTIR) spectrometer (Jasco FT/IR-6100V, Japan). Reflectance measurements were carried out in the mid infrared region (500–4000 cm^{-1}) in order to confirm the presence of functional groups in thermally oxided samples and in autoclave sterilized samples (three replicates). Electron spectroscopy for chemical analysis (ESCA) was utilized for surface composition and depth profile characterization. ESCA measurements were carried out using a Perkin–Elmer ESCA 5600 X-ray photoelectron spectrometer equipped with a monochromatic Al K_α source (1486.6 eV), operated at 13 kV and 400 W power. The extraction angle of a photoelectron was fixed at 45° and the base pressure in the vacuum chamber during measurements was $< 1 \times 10^{-8}$ Torr. A wide scan (1200–0 eV) was initially performed to obtain an overview of the surface composition. Narrow scans were performed at energy levels for interesting elements. For elemental depth profiling of the surface an ion gun of 3 kV