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Surface and mechanical properties of modified porous titanium scaffold

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ABSTRACT

The bioinertness makes surface treatments essential to improve the bioactivity of porous titanium scaffold, and surface treatment might affect their mechanical properties. So finding an optimum condition lying between bioactivity and mechanical properties seems to be curial. In this research, the effect of the time of the thermal oxidation at 600 °C on apatite formation and mechanical properties of the porous titanium scaffold was studied. The results of thin film X-ray diffraction and Raman spectroscopy indicated that the surface of heat treated samples up to 480 min was mainly covered by rutile. Also, wettability measurement and *in vitro* apatite formation ability assessment indicated that hydrophilicity and apatite formation ability of titanium surface could be increased with enhancing the time of heat treatment up to 240 min. While the mechanical properties of porous titanium scaffold had no significant change upon heating up to 240 min, further heating caused the reduction of mechanical properties. So, due to the mechanical properties of the porous titanium scaffold, the optimum time of thermal oxidation at 600 °C in atmospheric condition was 240 min for the surface treatment of the porous titanium scaffold.

1. Introduction

Titanium and its alloys have been extensively used in biomedical load bearing applications due to their low elastic modulus, high specific strength, excellent biocompatibility and superior corrosion resistance in physiologic mediums [1]. Despite these superiorities, some problems of titanium and its alloys in hard tissue applications are still controversial. For example, the mismatch of Young's modulus between titanium implants and the surrounding bones can be mentioned, leading to the 'stress shielding' phenomenon, which, in turn, can result in bone resorption and probable implant loosening. To overcome this drawback, porous metallic scaffolds have been introduced. The porous metallic scaffolds have less elastic modulus, close to that of human bone, thereby facilitating bone ingrowth and biological fixation; it can also provide better tissue nutrition around the scaffold [2]. Therefore, many studies have been conducted on the fabrication of porous titanium [3] and titanium alloys [4,5].

Also, titanium and its alloys are essentially bioinert materials [6] with no bone bonding ability; so upon implanting in the living body, they are merely encapsulated by the fibrous tissue. To alleviate this problem, some surface treatment techniques are introduced to improve the bioactivity of the surface of titanium [1,6] and titanium alloys [7].

Surface treatment of titanium can be divided in to three groups of mechanical (blasting, grinding, …), chemical (acidic, alkaline, …) and physical (thermal spray, sputtering, …) methods [1]. Only the surface treatment methods using fluid media are effective for the surface treatment of inner and outer pores of porous titanium scaffolds [8]. Direct oxidation has been performed on titanium scaffold by many researchers [9] to form bioactive phases on the surface of titanium. Air is also a fluid medium which can penetrate into the pores of the porous titanium scaffold and modify the surface of the inner pores. However, the effect of direct oxidation on the mechanical properties of porous titanium scaffolds has not been investigated.

With increasing the porosity, the mechanical properties of porous titanium scaffolds are decreased dramatically [10]. So, the elastic modulus (E) of most highly porous titanium has been reported to be less than that of the cortical bone (E = 1.6 GPa [11]). So it seems that improving the mechanical properties of surface modified porous titanium scaffolds can be a remarkable step in the future studies.

Leinenbach and Eifler investigated the effect of some different surface treatments on dynamic mechanical properties of two different rigid titanium alloys, and reported their differences. Based on their study, it was proposed that the surface treatment of titanium might affect its mechanical properties [13]. Also, according to our previous report, the mechanical properties of the porous titanium scaffold, due to hydrogen peroxide treatment, could be decreased because of its corrosive phenomenon, while alkali treatment has no significant effect on the mechanical properties of the porous titanium scaffold [13], both

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hydrogen peroxide and alkali treatments can lead to bioactive phase formation on the surface of titanium [13]. Also, Yavari et al. reported that different surface treatments affected the mechanical properties of the porous titanium scaffold significantly [14].

Therefore, the interplay between surface treatment and the mechanical behavior of porous titanium scaffold needs to be controlled. In this paper, we studied the effects of the time of direct thermal oxidation in atmospheric condition on the bonelike apatite inducement and the mechanical properties of porous titanium scaffold manufactured using the space holder method.

2. Materials and methods

2.1. Surface treated porous titanium scaffold preparation

2.1.1. Titanium scaffold fabrication

Space holder technique was used for manufacturing titanium scaffolds containing 70 vol% nominal porosity. Disc shape porous specimens with the diameter of 13 mm and the height of 2 mm (for *in vitro* bioactivity assessment),and cylindrical shape porous samples with the diameter of 13 mm and the height of 13 mm (for mechanical characterizations) were used. Also, disc shape rigid specimens (fabricated without spacer agent) with the diameter of 13 mm and the height of 2 mm were used for other assessments.

Raw materials including the commercially pure titanium powder (grade 2, the mesh size of 325, OSAKA Titanium Technologies Co., Japan) and Sodium chloride (the mesh size of 35–40, Wako Ltd., Osaka, Japan) as the spacer agent were blended; in the case of rigid samples, no spacer agent was used. Then they were compacted into the pellets by applying the uniaxial pressure of 200 MPa on the steel cylindrical mold. The cold compacted pellets were sintered through two stage sintering under vacuum (10^{-5} mbar) at the temperature of 800 °C for 2 h, and 1200 °C for 2 h (heating rate was adjusted at 5 °C/min). Finally, the sintered samples were cooled down in the furnace to room temperature. For salt leaching, samples were rinsed in distilled water for 35 h [3].

2.1.2. Titanium scaffold surface treatment

For direct thermal oxidation, porous and rigid samples were heated up to 600 °C at a rate of 5 °C/min using an electric furnace; then they were kept at 600 °C for 30, 60, 120, 240 and 480 min, and finally allowed to cool to room temperature in the furnace. The rigid samples heated for 0, 30, 60, 120, 240 and 480 min were named as RU R30, R60, R120, R240 and R480, and the porous samples heated for 0, 30, 60, 120, 240 and 480 min were named as PU, P30, P60, P120, P240 and P480.

2.2. Porous titanium scaffold characterization

2.2.1. Phase identification

To investigate phases formed on the surface of treated and untreated titanium samples, thin film X-ray diffraction (TF-XRD: SmartLab, Rigaku Co., Tokyo, Japan) was used as the radiation source Cu-Kα (Wavelength: $\lambda = 1.5405$ A°), at the rate of $2\theta = 1°$/min and the glancing angle of 1°, against the incident beam on the surface of the sample and in the range of $2\theta = 20–50°$.

Raman spectra were also recorded using Raman spectroscopy (Jasco, NRS-3200, Japan), typically in the range 100–780 cm^{-1}, using a $\lambda =$ 532 nm laser (green color) beam. The acquisition was realized with an exposure time of 600 s and 6 accumulations for each point, with an optical objective of ×100 and a diaphragm opening of 100 μm.

2.2.2. Microscopic observation

Scanning electron Microscope (SEM: JEOL, JCM-6000 Plus, Japan) and FESEM (JEOL, JSM-7500 FAM) were used to study the surface morphology of treated and untreated porous titanium samples. All samples were coated with gold (Au) before observation.

2.2.3. Elemental depth profile measurement

The surface of treated and untreated titanium samples was analyzed by an X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo Fisher Scientific, UK) equipped with a monochromatic X-ray source (Al-Kα) at 12 kV, 6 mA, under the pressure of 1.4×10^{-6} Pa. The spot size of the incident beam was set at 400 mm. The binding energies were normalized to the C1s peak of 284.80 eV. This test was performed to investigate the depth profile of oxygen on the surface of rigid heat treated samples.

2.2.4. Adhesive strength measurement

The adhesive bond/fracture strength of the oxide layer to the titanium substrate was measured using an adhesion test apparatus (ROMULUS IV, Epoxy Resin Adhesive, Quad Group Inc., USA). Stud-pins with 2.7 mm diameter were fixed on the surface of samples and then heated in an oven at 150 °C for 1 h to ensure hardening of the epoxy resin between stud- pin and the oxide layer. The stud-pin was pulled at a rate of 0.1 mm/s using a universal testing machine and the maximum load was recorded for each sample ($n = 5$) [15].

2.2.5. Wettability measurement

For wettability measurement, the water contact angle technique was used. A 10 μL droplet of distilled water was dropped onto the surface of treated and untreated titanium samples using the microsyringe system of contact angle instrument (FACE, CA-D). The shape of the droplet was observed and the contact angle was measured. This test was repeated five times for each sample and the mean value ± standard deviation was reported.

Although the main purpose of this research was investigating the effect of the time of heat treatment on the apatite formation ability and mechanical properties of porous titanium scaffolds, for surface phase identification, wettability and adhesive strength measurement, we had to use rigid titanium samples instead of the porous ones. The oxidation behavior of porous titanium samples and rigid ones was assumed to be the same.

2.2.6. Mechanical testing: porous samples

Compression test of porous surface treated and untreated titanium scaffolds was carried out in accordance with the ISO standard 13314:2011, with a constant deformation rate of 0.2 mm/min, using a universal testing machine (INSTRON 5566S, USA) and a mechanical testing machine (10 kN load cell). The plateau stress (σ_{pl}), as the arithmetical mean of the stresses between 20% and 40% compressive strain, was obtained for porous treated and untreated titanium scaffolds. Compression test of each sample was repeated three times, and the mean values were reported.

2.2.7. In vitro apatite formation ability assessment

The apatite formation ability was investigated by soaking the rigid and porous treated titanium samples into Dulbecco's phosphate buffered saline (DPBS: (Wako Ltd., Osaka, Japan) at 37 °C without stirring [16]. The solutions were refreshed every 48 h to maintain the ionic composition. After soaking for 7 days, the rigid and porous titanium samples were taken out from PBS, rinsed with distilled water and dried at 45 °C for 24 h. Finally, the surfaces were studied by SEM and TF-XRD.

3. Results and discussion

3.1. Phases identification

The thin film X-ray diffraction patterns (TF-XRD) for untreated (RU) and heat treated (R30, R60, R90, R120 and R240) rigid titanium samples are presented in Fig. 1. The RU, R30, R60, R90, R120 and R240 titanium rigid samples exhibited the titanium peaks at 2θ values of 35° and 40.15° (JCPDS No: 00-005-0682), corresponding to the pure titanium only. It could be seen that with increasing the time of heat treatment,