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## Fabrication of calcite-coated rough-surface titanium using calcium nitrate

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## ABSTRACT

Although Ti bone scaffolds are widely used clinically as various hard-tissue scaffolds including dental implants, their limited initial osseointegration property is a significant disadvantage, which should be improved. A rough surface and the allied Ca ion release capability might improve initial osteointegration by enhancing the activity of osteoblasts, which dominates osseointegration. In this study, a calcite-coating method, as a Ca ion releaser, is introduced onto rough surfaces of the Ti scaffold by heat carbonation using calcium nitrate as the Ca source below the  $\alpha$ -to- $\beta$  phase transition temperature ( $\sim 880$  °C) of Ti. After this treatment, the Ti scaffolds become whiter with increasing the concentration of the calcium nitrate solution. X-ray diffraction (XRD) and spectroscopic measurements demonstrate that calcite is formed on the Ti scaffold after the treatment. Scanning electron microscopy (SEM) observations show numerous rhombohedral crystals with a size of several micrometers, densely covering the surface of the Ti scaffold, maintaining its rough surface structure. Optimization of the initial calcium nitrate solution concentration controls the amount of calcite coating onto the desired regions on the surface of the Ti scaffolds. The coating strength of the fabricated calcite is  $\sim 20$  MPa, which is sufficient to resist implanting strength.

## 1. Introduction

Ti and its alloys, such as Ti-6Al-4V, are widely used as hard-tissue scaffolds, such as bone scaffolds, surgical bolts, artificial joints, dental implants, and spinal gauges, because of their excellent biocompatibility and physico-chemical properties. Approximately, several tens of million people globally receive the benefit of the Ti scaffold every year [1–4].

Ti is used as a bone scaffold because it can directly connect to the bone tissue and attract it to the surrounding Ti regions when it is implanted into the bone, which is known as its osseointegration property [5–7]. However, the drawback of Ti is that its osseointegration property and its bone-contact ratio are limited; therefore, failure of the implanted tissues often occurs [8,9]. In particular, its low initial osseointegration property should be improved for future clinical use. [8,10–12].

Various studies have been performed to overcome the drawbacks of Ti and improve its biocompatibility. For example, when a rough textured surface is integrated on the Ti substrate, its osseointegration property is significantly increased [8,13–15]. In addition, the initial osseointegration property dominates the activity of cells acting in the bone-remodeling process. Their activities are closely related to the Ca

concentration in the surrounding microenvironment of scaffolds [16–18]. In fact, Chen et al. [19] suggested that Ca ions released from implanted materials can enhance the activity of cells dominating the bone-remodeling process by stimulating their bone matrix protein 2 (BMP2) signaling pathway. Moreover, Hong et al. [20] reported that when a suitable amount of Ca is released from the alloy, it enhances the activity of rat osteoblastic cell-obtained rat calvaria bone marrow (MC3T3-E1 cell) in vitro.

Calcite is a polymorph of calcium carbonate found as a robust crystal with relatively high solubility under physiological conditions [21–23]. In addition, calcite itself has been already used as a bone substitute, revealing excellent initial osteoconductivity and bone-replacing rate [24–26]. Liu et al. [27] demonstrated a calcium carbonate-coated Ti plate, using a calcium carbonate precipitation method on a Ti plate immersed in a  $\text{CaCl}_2$  aqueous solution by exposing it to a  $(\text{NH}_4)_2\text{CO}_3$  stream. Although the calcium carbonate coating using the precipitation method enhanced the activity of osteoblastic cells, the coating shape and the amount of calcium carbonate were not very well regulated.

Therefore, in this study, we focus on establishing a method for generating uniform calcite coatings with Ca amount regulation using a

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calcium nitrate solution as a starting material. Treated Ti substrates with rough-textured surfaces were coated with calcite, maintaining the underlying roughness through a thermal carbonation process.

## 2. Material and methods

### 2.1. Materials

Commercial pure Ti (bare Ti) plates (T&I Co., Japan) squares with an area of 100 mm<sup>2</sup> were used as the coating substrates. Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Wako Pure Inc., Co., Japan) was dissolved in 99.5% ethanol (EtOH) to obtain 0.5, 1.0, and 2.0 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O-EtOH solution as the Ca source.

### 2.2. Acid etching of bare Ti

A bare Ti plate was immersed in a cocktail acid solution of 50 v% H<sub>2</sub>SO<sub>4</sub> and 7 v% HCl at 70 °C for 30 min to obtain etched texture on its surface. After acid etching, the etched Ti plate (Etched Ti) was washed in ethanol (70%) with ultrasonic treatment for 5 min and then washed in distilled water with ultrasonic treatment for 5 min. After washing, Etched Ti was placed at room temperature for drying.

### 2.3. Heating treatment for carbonation

For this, 5 μL of 0.5–2.0 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O-EtOH solutions were dropped onto the center of Etched Ti, following which the solvent was evaporated at room temperature to obtain the Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O precipitate on the Etched Ti surface.

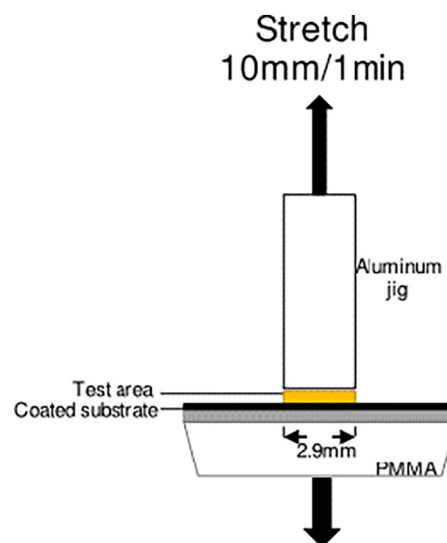
After the treatment by the Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O-EtOH solutions, Etched Ti and a control sample of Etched Ti without treatment were placed into an electric furnace (Mini-1, Nitto Kagaku Co., Japan) with a modified step controller (NPC-T03, Nitto Kagaku Co., Japan). The temperature of the furnace was increased from the room temperature to 550 °C at 3 °C/min and then maintained at 550 °C for 5 h with a CO<sub>2</sub> gas flow of 100 mL/min. Subsequently, the samples were cooled down inside the furnace.

### 2.4. Characterization

The surface materials obtained by the treatments were characterized by X-ray diffraction (XRD; D08 ADVANCE, Bruker AXS GmbH, Germany) at an acceleration voltage of 40 kV and a current of 40 mA using a Cu target. The 2θ range measurement was from 10° to 70° with an increment of 0.02°; the time per step was 3°/min. The samples were placed onto the XRD stage without any further treatment.

The surface morphology of the samples was observed by scanning electron microscopy (SEM; S-3400 N, Hitachi Hightech Co., Japan) at an acceleration voltage of 15 kV after Au/Pd sputter coating by a magnetron sputtering device (MSP-1, Vacuum Device Co., Japan). The elemental mapping of the samples was performed using energy-dispersed X-ray spectroscopy (EDX; EDAX GENESIS4000, EDAX Japan Co., Japan) combined with SEM at an acceleration voltage of 15 kV. The surface elemental analysis was performed and the coating structure was obtained using an X-ray photoelectron spectrometer (XPS: K-Alpha, ThermoFisher Scientific Co., USA) equipped with a monochromatic X-ray source (Al-Kα) at 12 kV, 6 mA under a pressure of 1.4 × 10<sup>-6</sup> Pa. The spot size of the incident beam was set to 400 μm. The binding energies were normalized to the C1s peak of 284.80 eV. The surface chemical bonding structure of the samples was determined by laser Raman spectroscopy (Raman: NRS-3100CS, Jasco Co., Japan) using a GaAs laser (wavelength: 784 nm) and a charge coupled device (CCD) detector (two accumulate scans, resolution: 0.02 cm<sup>-1</sup>). In the XPS and Raman measurements, reference CaCO<sub>3</sub> was used, a calcite single crystal obtained from *Saidosho-Mine, Kaharu-cho, Fukuoka, Japan*.

For material reaction estimation during the heat treatment, the



Scheme 1. Schematic image of the detaching test.

samples were measured using thermogravimetric analysis (TG-DTA; EXSTAR TG/DTA6300, SII Nano Technology Inc., Japan) under a stream of air or CO<sub>2</sub>. The heating rate was the same as that of the sample fabrication.

The surface roughness  $R_a$  of the samples was measured by surface roughness-measuring machines (SJ-400, Mitutoyo Co., Japan). An average value of  $R_a$  was calculated from a line on each sample ( $n = 5$ ).

An adhesion test apparatus was used to measure the adhesive bonding strength of the coating and the Ti substrate. The scheme of the measurement is shown in Scheme 1. A commercial cylindrical aluminum rod of 2.9 mm in diameter was attached to the surface of the sample by a thin layer of epoxy resin (Araldite AR-1600, Hantzman Co., Switzerland). The rate of stretching was controlled at 10 mm/min by a universal testing machine (AGS-J, Shimadzu Co., Japan). The maximum load was recorded until the rod detached from the surface of the sample ( $n = 4$ ). After the measurement, the surfaces of the samples were observed by SEM.

## 3. Results

Fig. 1. summarizes the TG-DTA curves of the thermal gradient and time evolution at ~550 °C of Etched Ti without Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in an air stream (a, b) and in a CO<sub>2</sub> flow (c, d) as well as with Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in an air stream (e, f) and in a CO<sub>2</sub> flow (g, h). In the case of Ti without Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, either in air or CO<sub>2</sub>, neither a slight weight change nor thermal differentiation was observed. Whereas, in the case of Ti with Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, either in air or CO<sub>2</sub>, three significant weight loss steps at around 80–120, 120–150, and 500–550 °C, corresponding to moisture evaporation, crystal water evaporation, and Ca(NO<sub>3</sub>)<sub>2</sub> decomposition, respectively, were observed. The TG-DTA analysis also indicated that at least 1 h is required for complete decomposition of Ca(NO<sub>3</sub>)<sub>2</sub> at ~550 °C.

Fig. 2. shows the photographs of bare Ti (a) and Etched Ti before the heat treatment (b), Etched Ti after the heat treatment without Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (c), with 0.5 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (d), with 1.0 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (e), and with 2.0 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (f). Bare Ti has a greyish smooth surface with bright metallic luster, whereas Etched Ti shows a dark brown-colored surface without any metallic luster. Although the surface color was essentially the same after carbonation without Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution treatment, the color of the Etched Ti samples after carbonation with the 0.5 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O solution treatment was revealed to be uniformly whitish. Furthermore, in addition to this tendency, a scaly texture which pseudomorphic remain of

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