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Effect of spatial design and thermal oxidation on apatite formation on Ti–15Zr–4Ta–4Nb alloy

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Abstract

Apatite formation on the surface of titanium and its alloys is effective for inducing osteoconductivity when implanted in bony defects. The aim of this study was to investigate the effects of thermal oxidation on apatite formation in macro-grooves on Ti–15Zr–4Ta–4Nb. Thermal oxidation at 500 and 600 °C in air led to modification of the Ti–15Zr–4Ta–4Nb surface to rutile phase titanium oxide. Ti–15Zr–4Ta–4Nb thermally oxidized at 500 °C in air showed no changes in metallographic structure, but not at 600 °C. After soaking in a simulated body fluid for 7 days, the formation of apatite could be observed on the internal surfaces of macro-grooves 500 μm deep and wide on Ti–15Zr–4Ta–4Nb thermally oxidized at 500 and 600 °C in air. These results indicate the potential for osteoconductivity of Ti–15Zr–4Ta–4Nb without changing its metallographic structure, by fabricating only the macro-grooves, i.e., spatial design, and by performing thermal oxidation at 500 °C.

Keywords: Titanium alloy; Apatite; Bioactivity; Thermal oxidation; Macro-grooves

1. Introduction

Osteoconductivity, which means bone growth on a materials surface, is one of the most desirable characteristics in the development of novel titanium-based implants. Various surface treatments have been proposed to provide osteoconductivity to titanium and its alloys, with the potential for apatite formation related to osteoconductivity. Currently, the most popular surface treatment for commercial artificial joints and dental implants is plasma-spray coating with hydroxyapatite. Plasma-sprayed hydroxyapatite on titanium has been reported to show beneficial effects such as osteoconductivity and direct-bone bonding ability [1]. However, the process has disadvantages attributed to the high temperatures used during the process, such as the possibility of fracture at the interface between the titanium and the hydroxyapatite due to the residual stress at the interface, and changes in the composition, porosity, crystallinity, and structure of the plasma-sprayed hydroxyapatite [2]. Several chemical treatments with NaOH [3,4] or H_2O_2 solutions [5,6] have also been reported to provide spontaneous apatite-forming ability to titanium metals in the body environment. These treatments produce Ti–OH groups in a titania hydrogel layer on

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the titanium surface that have a catalytic effect, triggering heterogeneous nucleation of apatite in simulated body fluid (SBF) [7,8]. SBF has an ion concentration almost equal to that in human blood plasma and is used to evaluate the potential of bone-like apatite layer formation in an in vitro examination. Our research group previously reported that two pieces of pure titanium covered with rutile due to thermal oxidation at 400 °C set together in a V shape with varied mouth openings induced apatite formed on both facing surfaces in SBF when the open mouth spaces were approximately 600 μm [9]. A pure titanium specimen with machined macro-groove of 500 μm in depth and 200–1000 μm in width followed by thermal oxidation at 400 °C also showed apatite formation in the internal space of the grooves [10,11]. These findings provide evidence that controlling both appropriate specific spaces and thermal oxidation temperature could enhance the potential for apatite formation on titanium. If we can clarify the appropriate conditions for the designed space on, and thermal oxidation of, titanium alloys, then this novel technique can be expected to provide apatite-forming ability to artificial joints and dental implants through a simple process, while maintaining high mechanical properties.

Ti–15Zr–4Ta–4Nb has been reported to show much better corrosion resistance, mechanical properties, and cytocompatibility than Ti–6Al–4V alloy [12]. Although living bone seems to come close to the surface of the Ti–15Zr–4Ta–4Nb [13], it does not show osteoconductivity because the biological affinity of the alloy is regarded as bioinert. In this study, the efficacy of our novel technique was examined using Ti–15Zr–4Ta–4Nb alloy. To clarify the appropriate temperature for thermal oxidation, the effect of the thermal oxidation temperature on the surface and metallographic structure of Ti–15Zr–4Ta–4Nb was examined, as was the apatite-forming ability of the alloy with macro-groove after soaking in SBF.

2. Materials and methods

2.1. Specimen preparation

Ti–15Zr–4Ta–4Nb alloy (Zr 15.36, Ta 3.95, Nb 3.95, Pb 0.18, Fe 0.26, O 0.23, N 0.04, Ti res. %) was prepared through a vacuum arc-melting process according to previous reports [12–14]. After β and α–β forging, the alloy was annealed for 2 h at 700 °C. For characterization of the surface and metallographic structure of the Ti–15Zr–4Ta–4Nb after thermal oxidation, rectangular specimens were cut to $10 \times 10 \times 3\ mm^3$, and ground with SiC abrasive paper up to #2000 (0.126 ± 0.02 μm Ra, SURFTEST SV-3000, Mitsutoyo Corporation). The prepared specimens were washed in an ultrasonic cleaner in ultrapure water and acetone for 30 min each. Specimens $12 \times 12 \times 5\ mm^3$ in size and with machined macro-groove of 500 μm in both depth and width were prepared in a manner similar to that described above [11]. These specimens were thermally oxidized at 200, 400, 500, 600, and 800 °C for 1 h in air using a muffle furnace, and then cooled down at room temperature outside of the furnace in air.

2.2. Surface characterization of the specimens after thermal oxidation

The surfaces of the rectangular specimens thermally oxidized at various temperatures were characterized by thin-film X-ray diffraction (TF-XRD; RINT2500HF+, Rigaku Corporation, Tokyo, Japan), laser Raman spectroscopy (NRS-1000, JASCO Corporation, Tokyo, Japan), and X-ray photoelectron spectroscopy (XPS; JPS-9000MC, JEOL Ltd., Tokyo, Japan). TF-XRD measurements were performed with a fixed time scanning mode with 0.02° steps and 1.0 s at each step using a Cu Kα X-ray source. In the laser Raman spectroscopic measurements, a single monochromator was used to obtain Raman spectra that were excited at 532 nm by a green laser. The XPS measurements were performed with Al Kα X-ray source with a take-off angle of 90°.

2.3. Characterization of the metallographic structure of the specimens after thermal oxidation

To observe the metallographic structure of the Ti–15Zr–4Ta–4Nb after thermal oxidation, rectangular specimens were embedded in epoxy resin, and then polished in cross-section using abrasive paper and a colloidal silica suspension. The polished surface of the cross-section was observed by scanning electron microscope (SEM; S-3000H, Hitachi Co., Ltd., Tokyo, Japan) with a back-scattering detector. A fraction of the α-phase of the Ti–15Zr–4Ta–4Nb was evaluated from each SEM image using image analysis software (ImageJ, National Institute of Health, Bethesda, MD, USA). Determination of the fraction of the α-phase (hexagonal close packing, hcp) was performed by ascribing the black regions in the SEM images to the α-phase of the Ti–15Zr–4Ta–4Nb. The fraction of the α-phase was calculated by dividing the area of α-phase obtained from binary SEM images by total area of SEM images.

2.4. Evaluation of apatite formation

To examine apatite-forming ability, thermally oxidized specimens with macro-grooves were soaked in 30 cm^3 of SBF at pH 7.40 at 36.5 °C (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0, and SO_4^{2-} 0.5 mmol dm^{-3}). The machined surfaces of the specimens were placed face down on the bottom of flat-bottomed polystyrene bottles when examining the designed space. SBF was prepared by following the method developed by Kokubo and colleagues [7,8]. After soaking in SBF for 7 days, the specimens were removed from the SBF, washed gently with ultrapure water, and dried at room temperature. The surfaces in the macro-grooves were observed by field emission scanning electron microscope (FE-SEM,

ID	Title	Pages
2369	Effect of spatial design and thermal oxidation on apatite formation on Ti–15Zr–4Ta–4Nb alloy	7