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Hydrothermal treatment of titanium alloys for the enhancement of osteoconductivity

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ABSTRACT

The surface wettability of implants is a crucial factor in their osteoconductivity because it influences the adsorption of cell-attached proteins onto the surface. In this study, a single-step hydrothermal surface treatment using distilled water at a temperature of 180 °C for 3 h was applied to titanium (Ti) and its alloys (Ti–6Al–4V, Ti–6Al–7Nb, Ti–29Nb–13Ta–4.6Zr, Ti–13Cr–1Fe–3Al; mass%) and compared with as-polished Ti implants and with implants produced by anodizing Ti in 0.1 M of H_3PO_4 with applied voltages from 0 V to 150 V at a scanning rate of 0.1 V s^{-1}. The surface-treated samples were stored in a five time phosphate buffered saline (×5 PBS(−)) solution to prevent increasing the water contact angle (WCA) with time. The surface characteristics were evaluated using scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, Auger electron spectroscopy, surface roughness, and contact angle measurement using a 2 μL droplet of distilled water. The relationship between WCA and osteoconductivity at various surface modifications was examined using in vivo tests. The results showed that a superhydrophilic surface with a WCA ≤ 10° and a high osteoconductivity (R_{B-I}) of up to 50% in the cortical bone part, about four times higher than the as-polished Ti and Ti alloys, were provided by the combination of the hydrothermal surface treatment and storage in ×5 of PBS(−).

1. Introduction

Approximately 70–80% of implants are manufactured from metallic biomaterials, such as stainless steels, cobalt–chromium alloys, and titanium (Ti) and Ti alloys [1]. Among them, Ti and Ti alloys indicate the highest biocompatibility, corrosion resistance, and specific strength (ratio of tensile strength to density) compared with stainless steel and cobalt–chromium alloys. The Ti–6Al–4V (Ti64) alloy of the α + β type has been used widely as a high-strength biomedical alloy. However, the possible toxic effect of the released vanadium (V) ions on the human body has created some concern [2–4]. The V-free Ti alloys, such as Ti–6Al–7Nb (Ti67) (α + β type), were introduced into clinical use as a substitute for Ti64 because, as noted, the V ions in practical Ti64 were toxic [5]. Nowadays, β-phase Ti alloys, such as Ti–29Nb–13Ta–4.6Zr (TNTZ) and Ti–13Cr–1Fe–3Al (TCFA), have been introduced for implant biomaterials because the values of the Young's modulus for these Ti alloys are smaller than the Young's modulus for the α-phase or (α + β)-phase Ti alloys [6–8]. The use of β-phase Ti alloys as bone substitutes is expected to overcome the bone resorption caused by the stress shielding effect.

However, Ti and Ti alloys are recognized as bioinert materials due to the lack of direct chemical bonding to the host bone tissues after implantation. Therefore, as a way to improve their osteointegration, surface modification has become essential [9]. Anodization is one of the most popular surface modification techniques to improve the osteoconductivity of Ti and Ti alloys by producing a Ti oxide layer. However, this process is not effective for all types of Ti alloys. Yamamoto et al. reported that anodizing did not enhance the osteoconductivity of TNTZ and TCFA, although it can be improved on pure Ti and the Ti64 and Ti67 alloys [10].

Recently, hydrothermal treatment has attracted attention in the synthesis of functional materials, such as $BaTiO_3$, ZrO_2, and TiO_2 [11,12]. In our previous study, we applied a hydrothermal treatment for the surface modification of metallic biomaterials, compared with ultraviolet irradiation and plasma irradiation. It is reasonable to use hydrothermal treatments on biomaterials with complex shapes and topographies because of line-of-sight application. Our previous study also reported that the osteoconductivity of pure Ti could enhance its osteoconductivity effectively by producing a hydrophilic surface after hydrothermal treatment without anodizing [13]. Therefore, in this paper, a single hydrothermal surface treatment on Ti alloys was performed to confirm

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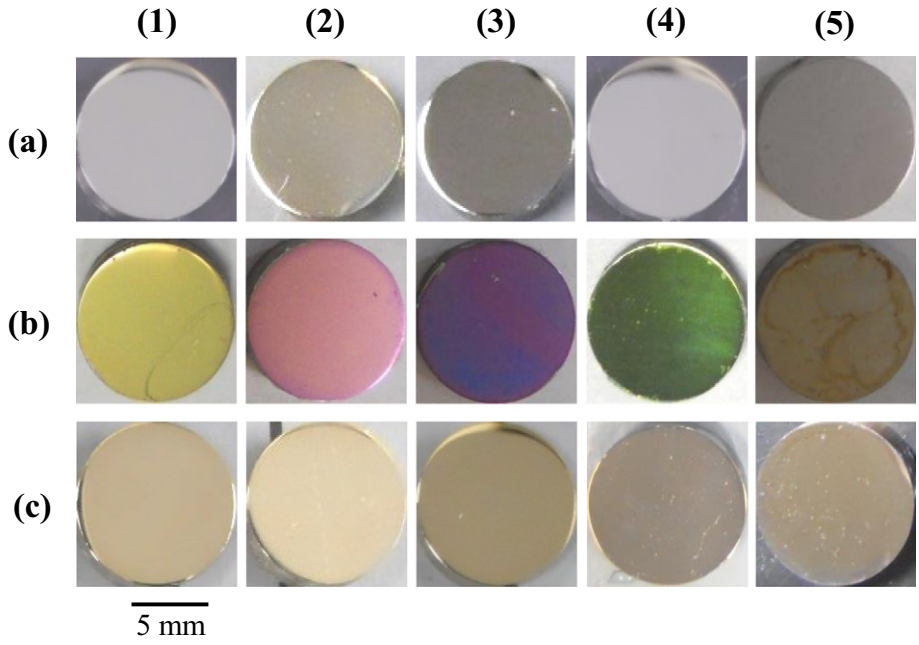

Fig. 1. Photographs of samples of (1) Ti, (2) Ti64, (3) Ti67, (4) TNTZ, and (5) TCFA, each of which was (a) polished, (b) as-anodized in H_3PO_4 solution, and (c) as-hydrothermaled in distilled water at 180 °C for 180 min.

whether the hydrothermal treatment was effective in improving the osteoconductivity, and optimum methods were considered to maintain the hydrophilicity of the alloys. The osteoconductivity was investigated using in vivo tests.

2. Materials and methods

2.1. Materials preparation

Two different sample shapes made from pure Ti, Ti64, Ti67, TNTZ, and TCFA were used to characterize the surface and to evaluate the osteoconductivity in the in vivo tests. Plates with the dimensions of 12 mm × 4 mm were used for surface characterization, and rods with a diameter of 2 mm and length of 5 mm were used for in vivo tests. The samples were classified into the following three groups: Group I, as-polished; Group II, as-anodized; and Group III, as-hydrothermally treated. All samples were abraded with emery papers up to #2000, polished by Al_2O_3 particles of 0.05 μm in size, degreased with ethanol for 5 min in an ultrasonic cleaner, and finally dried at room temperature. In Group II, anodizing was performed using a final voltage of 100 V (65 V for TCFA) at a rate of 0.1 V s^{-1}. The electrolyte solution was 0.1 M of H_3PO_4 and this was stirred using a magnetic stirrer at a constant temperature (25 °C) in a water bath during anodizing. After anodizing, the specimens were sterilized using an autoclave unit at 121 °C for 20 min. In Group III, hydrothermal treatment was carried out for the Group I as-polished specimens using 300 ml of distilled water in a hydrothermal unit at a temperature of 180 °C for 180 min.

It has been reported that storage environment has a notable effect on the surface hydrophilicity of the material [14]. Therefore, the specimens were stored under two storage environments (at room temperature), namely in air and in five times concentrated phosphate buffered saline (×5 PBS(−)). The composition of ×1 PBS(−) was (in g l^{-1}) 8 NaCl, 0.2 KCl, 1.44 Na_2HPO_4, 0.24 KH_2PO_4, and <0.1 diethyl dicarbonate. The storage period of the samples in the different media was up to

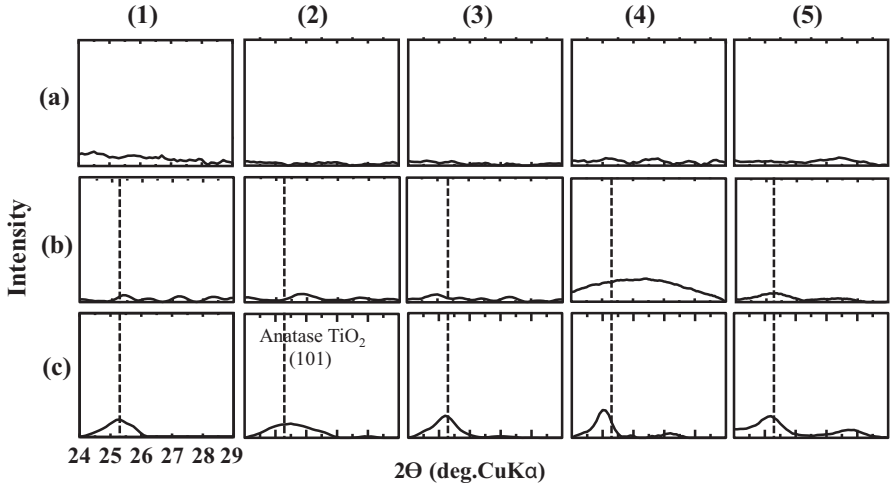

Fig. 2. XRD patterns of (1) Ti, (2) Ti64, (3) Ti67, (4) TNTZ, and (5) TCFA using different treatments: (a) polished, (b) as-anodized in H_3PO_4 solution, and (c) as-hydrothermaled in distilled water at 180 °C for 180 min.