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Short communication

Biomimetic formation of calcium phosphate on thermally oxidized cp-titanium surfaces

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Abstract

Commercially pure titanium disks as-received and heat treated at 600 °C in air for 10 min were used to investigate differences in calcium phosphate forming ability. X-ray diffraction, field emission–scanning electron microscopy and energy dispersive X-ray spectrometry were used to collect information on surface properties. Sample with an amorphous TiO_2 layer after heat treatment showed high CaP forming ability.

Keywords: Titanium; Calcium-phosphate

1. Introduction

Chemical treatment or combined chemical and heat treatments [1,2] are simple and effective techniques to prepare osteoconductive titanium surface. These procedures have widespread use in the preparation of biomimetic apatite coatings and in the assessment of the osteoconductivity of biomaterial surfaces.

It is shown that, in human cementless total hip arthroplasty (THA), osteointegration is not always achieved on smooth-surfaced titanium metals [3]. If smooth titanium metals have an ability to bond to bone without forming intervening fibrous tissues, cementless THA implants may be able to achieve long-term stability without porous coatings such as sol–gel derived TiO_2.

In this work, *in vitro* test was performed to investigate the difference in potential bone conductivity between untreated and only heat-treated titanium, i.e., the effect on the calcium phosphate (CaP) forming ability of thermally oxidized TiO_2 thin film. We selected mirror-polished titanium samples to avoid surface roughness effects by applying a different polishing process. Our results will therefore be useful for comparison with experiments on implants with rough surface.

2. Experimental

Commercially pure titanium (cp-Ti, NKK Co., Japan) disks 14 mm in diameter and 1.5 mm thick ground with SiC sand papers and then polished with alumina powders (up to 0.05 μm) were used.

To prepare TiO_2 films, the cleaned disks were heat treated at 600 °C for 10 min in air. CaP forming ability was tested in Eagle's minimum essential medium solution (MEM, Gibco BRL, Life Technologies, USA). Untreated as-polished and heat-treated samples were immersed for up to 30 days in 15 mL MEM solution at 36.5 °C.

X-ray diffraction (XRD, D-Max-1200, Rigaku Co., Japan) analysis was used to determine the degree of crystallinity of the surface. Also, surface morphology and the composition were examined by field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Japan) and energy dispersive X-ray spectrometry (EDX, S-4700, Hitachi Co., Japan).

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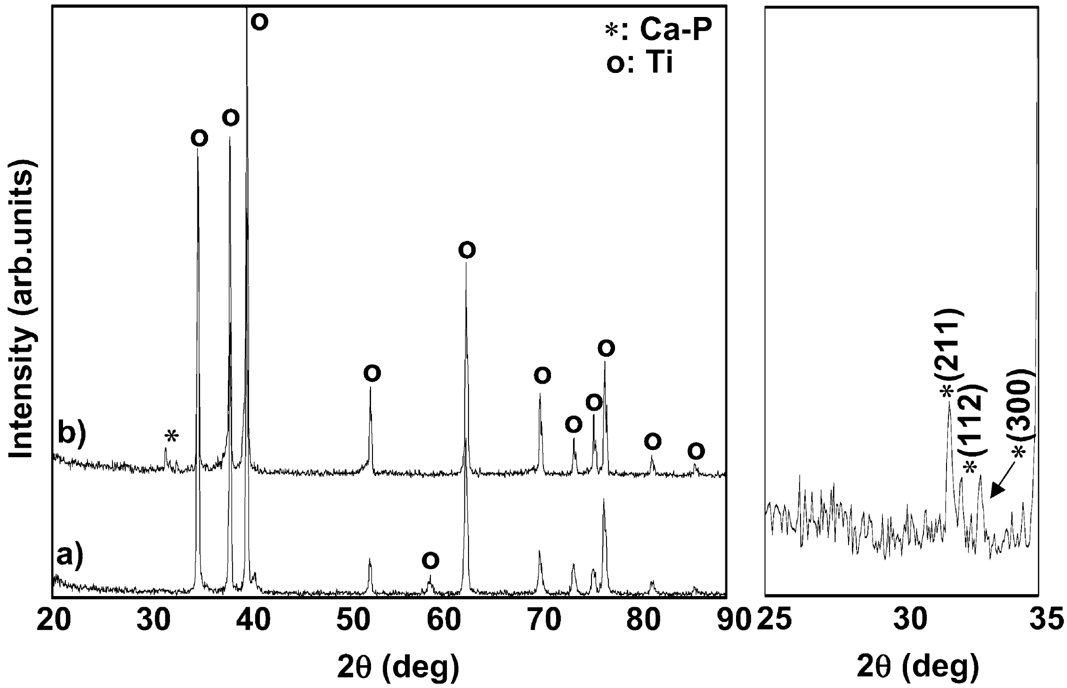

Fig. 1. XRD pattern after immersion in SBF of the untreated (a) and 600 °C-heat treated (b) titanium samples.

3. Results and discussion

Fig. 1 shows the XRD pattern of the untreated (a) and heat-treated (b) samples after soaking. As shown in Fig. 1(a), peaks corresponding to the titanium alone were observed. In Fig. 1(b), faint peaks belonging to the HAP structure were visible. After immersion, HAP peaks corresponding to the (211), (112) and (300) reflections were identified at the surface of the heat-treated sample (right panel of Fig. 1).

In addition, FE-SEM and EDX analyses were performed on the samples before [Fig. 2(a) and (b)] and after [Fig. 3(a)–(d)] immersion. As shown in Fig. 2(a), as-polished sample showed a smooth mirror-like surface. On the other hand, the sample heat treated at 600 °C [Fig. 2(b)] exhibited a heterogeneous surface morphology.

Fig. 3 shows FE-SEM micrographs of untreated (a) and heat-treated (c) titanium surfaces after soaking. There was no CaP formation as well as precipitation of other ions such as Mg, Na and Cl from the MEM solution at the surface of untreated sample [Fig. 3(b)]. However, formation of an unknown coating was clearly visible at the surface [Fig. 3(a)], although its composition could not be identified by EDX. The calcium and phosphate ions required for hydroxy apatite generation on the TiO_2 surface were derived from the MEM solution. This was indicated by an increase of the concentrations of phosphate and calcium ions on TiO_2 [Figs. 3(c) and (d)].

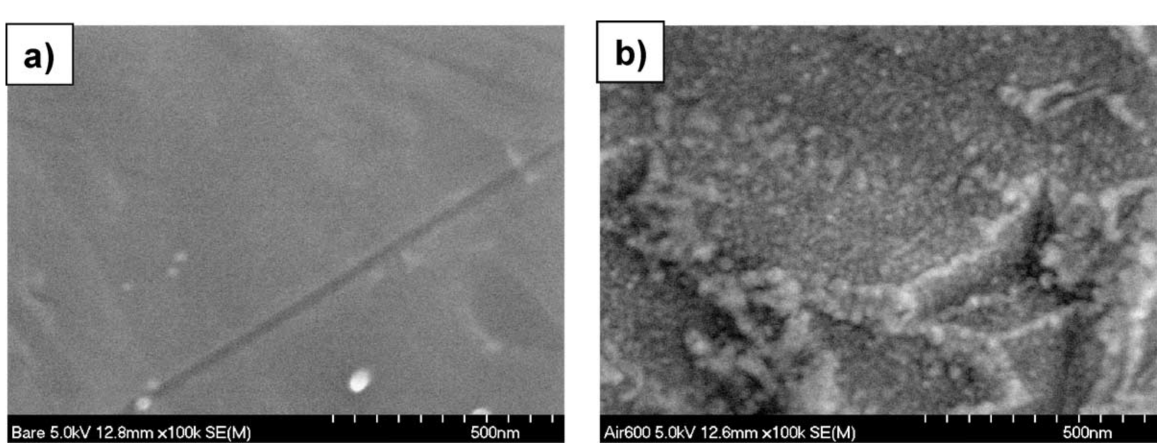

Fig. 2. FE-SEM micrographs of untreated (a) and 600 °C-heat treated (b) titanium samples before immersion.

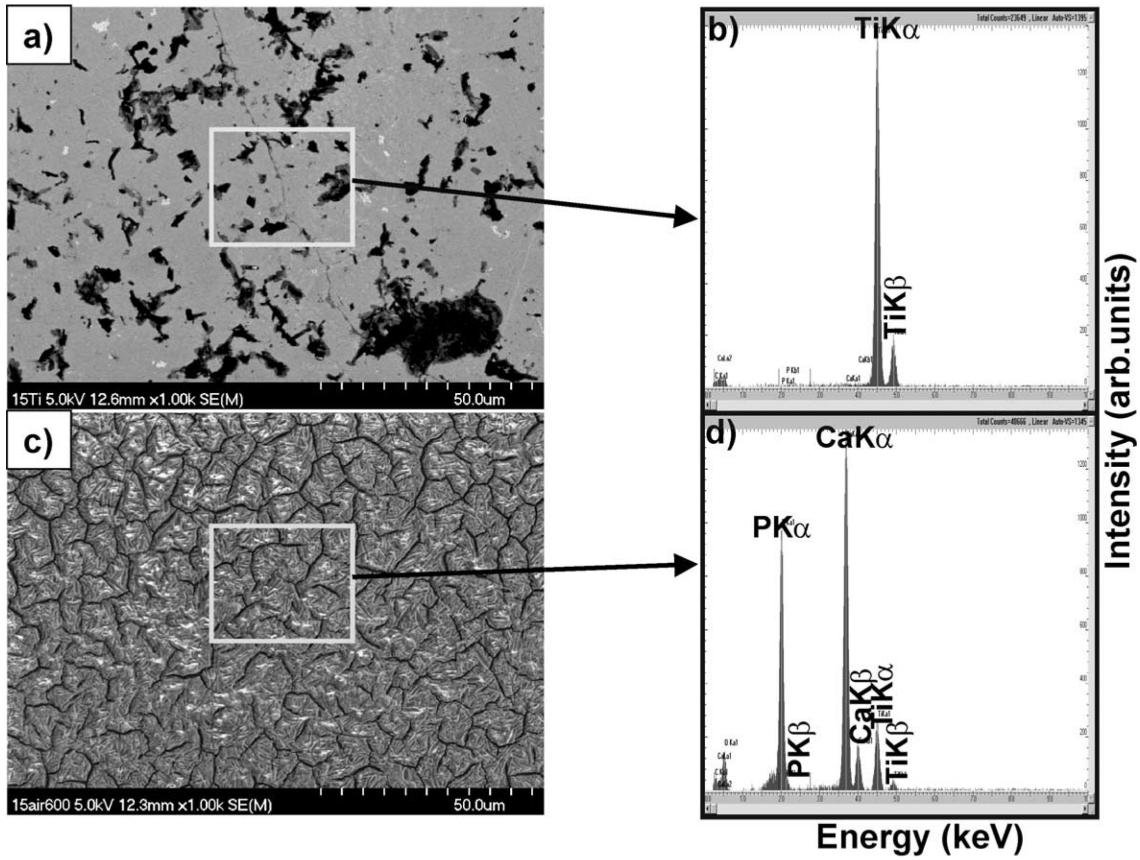

Fig. 3. FE-SEM micrographs and chemical compositions of untreated (a) and (b), and 600 °C-heat treated (c) and (d) samples, respectively, after immersion.

The first step in the nucleation of hydroxy apatite in the presence an osteoconductive oxide is thought to be an electrostatically driven adsorption of Ca^{2+} ions at ionized surface hydroxyl groups onto which phosphate is subsequently adsorbed [3,4]. Amorphous TiO_2 has been shown to hydrolyze readily in simulated body fluid (SBF) [5]. Compared to a dense oxide film in solution, a porous surface is more open for ions to be incorporated through the pores into the oxides. In our work, a newly formed amorphous TiO_2 layer with a heterogeneous structure corresponding to porosity and surface area was probably responsible for the CaP forming ability of the heat-treated titanium.

4. Conclusion

CaP forming ability of cp-Ti samples with and without heat treatment was investigated. As confirmed by FE-SEM and EDX analyses, samples with an amorphous TiO_2 layer heat treatment showed high CaP forming ability, while the untreated titanium exhibited no CaP formation on its surface.

Acknowledgements

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