

The structure of titanate nanobelts used as seeds for the nucleation of hydroxyapatite at the surface of titanium implants

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Abstract

The sequence of steps of a chemical treatment having as its goal the induce of nucleation and the growth of hydroxyl carbonated apatite (HCA) at the surface of titanium implants was studied by scanning and transmission electron microscopy in cross-section. In the first step, an acid etching forms a rough titanium hydride layer, which remains unchanged after subsequent treatments. In the second step, soaking in an NaOH solution induces the growth of nanobelt tangles of nanocrystallized, monoclinic sodium titanate. In the third step, soaking in simulated body fluid transforms sodium titanate into calcium titanate by ion-exchange in the monoclinic structure. HCA then grows and embodies the tangled structure. The interfaces between the different layers seem to be strong enough to prevent interfacial decohesion. Finally, the role of the titanate structure in the nucleation process of HCA is discussed.

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1. Introduction

Titanium and titanium alloys are widely used for dental and orthopedic implants, due to their high mechanical strength and good biocompatibility. In addition to these characteristics, it is also crucial to ensure good osteointegration [1]. A current way to achieve suitable bone-bonding is to deposit a hydroxyapatite (HA) layer, with a composition similar to the mineral part of the bone, at the implant surface. Plasma spraying is the most used coating technique. However, since it provides only poor adhesion [2], alternative solutions have been developed. Interesting properties have been obtained in this respect after fairly simple chemical surface treatments. The principles of these treatments have been established by Kim et al. [3,4]. They are based on the chemical activation of the titanium surface during immersion in an NaOH solution and subsequent

heat-treatment. On the basis of scanning electron microscopy (SEM) observations and X-rays diffraction (XRD) analyses, these authors proposed the following sequence of transformations. First, the NaOH treatment generates an amorphous sodium titanate hydrogel layer, which subsequently transforms into fully crystallized sodium titanate (indexed as $\text{Na}_2\text{Ti}_5\text{O}_{11}$) and rutile through heat treatments. During in vitro bioactivity tests of the pretreated titanium in simulated body fluid (SBF), Na ions from the surface were observed to be released, followed by the growth of a hydroxyl carbonated apatite (HCA) layer. Further investigations by Takadama et al. [5,6], including transmission electron microscopy (TEM) observations, yielded more details on the release of Na ions in SBF prior to HCA nucleation and growth. These authors showed that about 30% of Na atoms are replaced by Ca atoms after 3 days in SBF, which has been interpreted as the partial transformation of the amorphous sodium titanate into amorphous calcium titanate. The possible existence of calcium titanate has not, however, been mentioned in further publications.

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Uchida et al. [7] subsequently discussed the effect of a more or less pronounced washing in water on the removal of Na atoms from the titanate layer. After complete elimination of Na atoms and subsequent high-temperature treatment, the sodium titanate layer has been shown to transform into anatase titanium oxide.

The same method has been used and improved by several groups. Wen et al. [8] and Jonasova et al. [9] aimed to increase the roughness of the initially polished titanium substrate surface by acid etching in HCl, before soaking in NaOH and SBF. This procedure not only allows the morphological desired effect to be obtained, but also induces, through the acid etching, the growth of a titanium hydride layer [10]. This may increase the efficiency of the subsequent NaOH treatment, according to Tanaka et al. [11]. The chemical effect involved is, however, not clearly understood.

Another debated topic is the origin of the easy growth of HCA induced by HCl and NaOH treatments. It has been interpreted in two alternative ways: (i) the formation of anatase (and, to a less extent, rutile) nanoparticles, which may enhance the epitaxial growth of HA [7]; and (ii) the presence of amorphous calcium titanate, which may promote HA growth on account of some chemical affinity [5,6].

Independently, sodium titanate nanobelts, nanorods and nanotubes have been extensively studied in view of various applications, including ion-exchange capability [12–21]. These structures are grown on TiO₂ particles by a process similar to that described above. They nucleate as Na₂Ti₃O₇ sodium titanate after NaOH treatment, and transform into first H₂Ti₃O₇, and then into monoclinic TiO₂ or anatase after various washing procedures (with or without HCl) and heat treatments. These studies have never been compared to those carried out on biomaterials to the authors' knowledge. They will be described more completely in the discussion section.

In all cases, the essential problem to be solved is the way in which HCA nucleates and grows on the treated Ti surface. To date, the process steps involved in obtaining biomimetic materials have generally been studied by SEM and XRD. A single study performed by TEM is reported in the literature by Takadama et al. [6], on titanium grids subjected to NaOH and SBF treatments. In these experiments, only the outmost part of the titanate structure (after NaOH treatment) and HCA layer (after soaking in SBF) could be observed and analyzed. Observations below the sample surface, at a depth of several micrometers, are possible only in thin foils prepared in cross-section, as in pre-

vious studies by Conforto et al. [10] and Muller et al. [22]. The same method is used in this article to analyze the transformations at the surface of a Ti substrate after etching with HCl, followed by the treatment in a NaOH solution and soaking in SBF.

2. Experimental

Commercially pure titanium plates with a thickness of 1 mm were etched using 37 wt.% hydrochloric acid (HCl) under a CO₂ atmosphere for 2 h at 50 °C. The goal of this etching was to dissolve the titanium oxide passivation layer and generate a homogeneous surface with an average roughness of 4 μm. The specimens were subsequently soaked in 10 mol l⁻¹ NaOH aqueous solution at 60 °C for 24 h, washed with distilled water and dried at 100 °C. Finally, samples were exposed to SBF solutions with a composition similar to human blood plasma (Table 1) under static conditions at 37 °C for 2 weeks, in order to obtain a homogeneous apatite layer. SBF solutions were prepared by adding concentrated solutions of KCl, NaCl, NaHCO₃, MgSO₄ · 7H₂O and KH₂PO₄, to double-distilled water buffered with tris(hydroxymethyl)aminomethane and HCl to pH 7.4 at 37 °C [23]. Sodium azide (NaN₃) was added to the solution to inhibit the growth of bacteria. After exposure, the samples were washed in double-distilled water.

The microstructure and elemental composition were determined by electron microscopy on samples at different steps of the treatment, namely: (i) after HCl etching; (ii) after additional soaking in NaOH solution; and (iii) after exposition of the resulting surface to SBF. SEM observations were carried out using two Philips/FEI microscopes equipped with an EDAX system: XL-30 FEG, operated in the 3–10 kV range, and Quanta 200 ESEM/FEG, operated at 20 kV and at variable pressure in the specimen chamber. TEM was performed with two JEOL JEM 2010 and 2011 apparatus operated at 200 kV. Bright-field images and selected area diffraction patterns were obtained from TEM cross-sectional specimens. Diffraction patterns were indexed using conventional methods (see e.g. [24]). To prepare them, two surfaces were joined with epoxy glue. The resulting sandwich was cut perpendicular to the original surfaces, mechanically polished and thinned to perforation by ion-milling using a GATAN Precision Ion Polishing System (PIPS apparatus), in complete rotation mode. The bombardment was performed using two beams of Ar⁺ ions with energy of 5 keV at low angle (7°), in order to obtain the largest thin area, from the substrate up to the surface.

Table 1
Comparison of the ionic concentrations in blood plasma and the theoretical one in SBF (mmol l⁻¹)

	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	HPO ₄ ²⁻	SO ₄ ²⁻
Blood plasma	142.0	3.6–5.5	1.0	2.1–2.6	95.0–107.0	27.0	0.65–1.45	1.0
SBF	142.0	5.0	1.0	2.5	126.0	10.0	1.0	1.0

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