



Controlled bioactivation of titanium disc: A constant composition kinetic approach



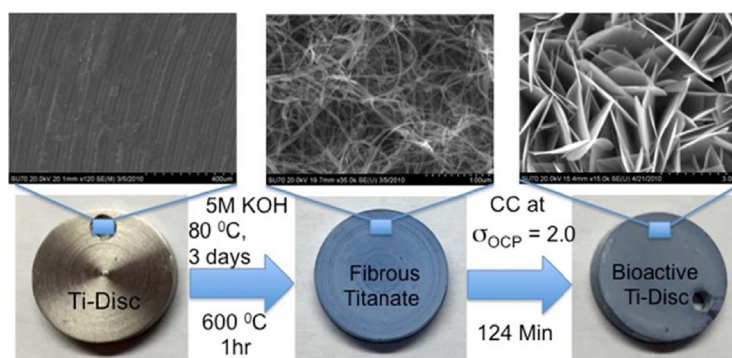
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HIGHLIGHTS

- KOH was more effective than NaOH for the bioactivation of titanium discs.
- At constant driving force OCP not HAP nucleated on the activated titane surface.
- Using CC the induction time controlled by adjusting the relative supersaturation.
- The mass of the Ca-P nucleated can controlled by the CC method.

GRAPHICAL ABSTRACT



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ABSTRACT

Titanium is widely used in orthopedic applications. To improve osseointegration, the surface composition and topography of pure titanium is often modified to impart bioactivity. These surface modifications typically involve coating titanium in a calcium phosphate mineral layer. This work presents a unique method for the well-controlled bioactivation of titanium discs. Using the constant composition (CC) method combined with scanning electron microscopy (SEM) Ca-P mineralization on titanium surfaces was studied across a range of thermodynamic driving forces (σ), and the effects of both KOH and NaOH used in the alkali treatment were investigated. Our findings indicate that the use of KOH in the alkali treatment of titanium discs is more effective in forming a fibrous titanate layer. The formation of a titanate layer promotes the formation of octacalcium phosphate [$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$, OCP] coating directly bound to the disc surface. These findings highlight importance of the alkali metal chosen in the base treatment of titanium discs, a critical step in several bioactivation processes.

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1. Introduction

Titanium is widely used as a dental and orthopedics implant material [1–4]. Titanium has many properties which make it a suit-

able for osseointegrations; high corrosion resistance, light weight, non-toxic, chemically inert, and mechanical properties similar to bone [5,6]. It has mechanical properties are closer to bone than stainless steel, or metal alloys containing cobalt or chromium [7]. The stable form of titanium at physiological pH is titanium dioxide. The oxide coating is 5–100 Å in thickness, and spontaneously forms when titanium is exposed to air [8]. The electrophoretic mobility, point of zero charge (p.z.c) and the acid/base nature at the titanium oxide interface with water, has been extensively studied [8].

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Table 1
Reaction conditions for nucleation experiments on titanium discs ($I = 0.15$ M, pH 7.40 at 37.0 °C).

Component concentration (mmol L ⁻¹)		Mole ratio	Relative supersaturation		dG (KJ)	
Calcium (as CaCl ₂)	Phosphate (as KH ₂ PO ₄)		$\sigma_{(\text{HAP})}$	$\sigma_{(\text{OCP})}$	HAP	OCP
0.98	0.59	[Ca]/[PO ₄] = 1.66	9.00	0.77	-5.94	-1.47
1.70	1.02		14.96	1.80	-7.14	-2.65
1.85	1.11		16.13	2.00	-7.33	-2.83

The investigations have shown that the interfacial tension between the TiO₂ surface and water is -11.7 mJ m⁻² [7,8], implying that the interface formed between TiO₂ and aqueous phases is thermodynamically unstable and that it would be less biocompatible when used as an implant directly. For these reasons it necessary to treat the implants in order improve bioactivity and impart bioactivity [9]. The bioactivation of titanium for bone replacements promotes the direct bonding of the implant to the bone surface without the formation of fibrous tissues [5].

Calcium phosphates have a high potential for attachment to osteoinductive agents compared to inert titanium and metal alloy implants [10–13]. Several different procedures have been reported for the formation of a calcium phosphate coating on a titanium surface including; electrochemical deposition, plasma spraying, ion-beam sputtering, surface-induced mineralization (SIM), and surface coating techniques such as sol-gel coatings on TiO₂, ceramics containing HAP, and glass-ceramic A–W [14,15]. These techniques produce coatings that are destroyed overtime eliminating the benefits in implant longevity [16,17].

The formation of calcium phosphates on titanium surfaces provides strong binding to bone; however calcium phosphate phases do not readily nucleate on these surfaces [18]. Surface roughening, chemical treatment, and heat treatment have been reported to improve the nucleation of calcium phosphate minerals on titanium surfaces [19]. Vatanatham and Kimura report both the rutile and anatase phases of TiO₂ are needed for the formation of a titanate layer by alkali and heat treatment [20]. Their use of chemical and heat treatment formed a sodium titanate layer on the titanium surface capable of nucleating strongly bound calcium phosphate minerals [20,21]. Subjecting TiO₂ to KOH treatment followed by heat treatment at 600 °C results in the formation of a potassium titanate layer; this layer is said to accelerate the deposition of HAP on the Ti surface [22,23]. When titanium is treated with KOH a hydrated titanium oxide gel layer containing potassium ions is formed on its surface. The sample is then heat treated (600 °C) to oxidize Ti forming an amorphous titanate layer. This produces the bioactive material which accelerates calcium phosphate deposition. The formation of apatitic phases as well as OCP has been reported using this procedure [5,24]. At biological pH OCP is a likely precursor to the formation of HAP on titanium surfaces [7,24].

Although it is known that this procedure accelerates calcium phosphate mineral deposition [20–23], no kinetic studies have been done on the heterogeneous nucleation and crystal growth of calcium phosphates on such surfaces. Constant composition (CC) kinetics is a valuable tool in elucidating mineralization phenomena [25–27]. By applying these techniques to the kinetics calcium phosphate mineralization in the presence of Ti discs, control over the rate of mineralization, induction time, and mass of nucleated material can be gained. This control is unique to the CC method, and has enabled the influence of the cation used in alkali treatment of the titanium disc to be investigated while varying only one aspect of the mineralization process.

2. Materials and methods

Titanium discs measuring 12.7 mm (0.50 in) in diameter by 2.00 mm (0.080 in) in height were machined from a titanium rod

(99.97%; Alfa Aesar), and were polished by hand using increasingly finer sandpaper until observable machining marks no longer were visible without magnification. Once polished, the discs were washed with methanol and ethanol to remove oils, and then rinsed with distilled water. Samples were treated in a bomb with 5 M KOH or NaOH solutions at 80 °C for 3 days, followed by 1 h at 600 °C.

2.1. Driving force and solution speciation

Solution speciation calculations were made to determine the relative supersaturations, σ , for mineral phases. These calculations were made using the extended Debye–Hückel equation proposed by Davies [28], with mass balance expressions for total calcium and phosphate incorporating appropriate ion pair equilibrium constants by successive approximation for the ionic strength, (Eq. (1)).

$$\sigma = S - 1 = \left[\frac{\text{IAP}}{K_{\text{SP}}} \right]^{\frac{1}{\nu}} - 1 \quad (1)$$

where IAP is the ionic activity product of free lattice ions in solution, K_{SP} the activity solubility product (HAP 2.21×10^{-117} mol¹⁸ L⁻¹⁸, OCP 2.51×10^{-99} mol¹⁶ L⁻¹⁶) [29,30] and ν the number of ions in a formula unit (HAP $\nu = 18$, OCP $\nu = 16$). Conditions used for the calculations are shown in Table 1. The aim of these calculations was to use the analytically determined total concentrations of calcium phosphate ionic components and estimate the extent of ion-pairing, as well as the mineral phases which form under these conditions.

3.1. Experimental method

Reactions were made in Teflon[®] covered, 150 mL double-walled Pyrex[®] jacketed cells, thermostated at 37.0 ± 0.1 °C by a circulating water bath. Supersaturated solutions were prepared under vigorous stirring conditions by the slow addition of sodium chloride (NaCl), potassium dihydrogen phosphate (KH₂PO₄), potassium hydroxide (KOH), and calcium chloride (CaCl₂) stock solutions ([Ca²⁺] = 0.040 M). The solution composition for different supersaturation experiments was shown in Table 1. To avoid a high local supersaturation as a result of the rapid mixing, a slower addition rate (200 μ L/min; Brinkmann Metrohm 775 Dosimat) was used for the addition of Ca²⁺ to the reaction solution. CO₂ was purged from the reaction vessel by constant bubbling of pure, presaturated, N₂ gas (>2 h) into both reaction solutions and calcium chloride stock solution prior to mixing. During crystallization experiments the pH was monitored by a glass electrode (Orion 91-01 ± 0.1 mv) coupled with a single-junction Ag/AgCl reference electrode (Orion 90-01). The resolution of the pH meter (Orion 720 A+) is 0.001 pH unit; the electrode was calibrated utilizing pH 6.841 and pH 7.385 phosphate buffers. After calibration, the electrodes were washed extensively with triple distilled water (TDW) and allowed to stabilize in the reaction cell. When a stable *emf* value had been reached, the automatic titrator potentiostat was set to this value (i.e. the “voltage bias”). As nucleation and growth took place, the removal of ions from the bulk solution caused a deviation in the cell solution concentration and *emf* from the set value. If greater than ± 0.050 mV, the addition of titrant solutions from mechanically coupled burets was triggered to restore the *emf* to the “voltage bias.” A computer

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