Gel Oxidation Of Titanium And Effect Of UV Irradiation On Precipitation Of Hydroxyapatite From Simulated Body Fluid

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Abstract. Sodium titanate gels on the surface of titanium metal have been formed using sodium hydroxide solution and oxidised at 400°-800°C. The reaction sequence for these processes with increasing temperature is Ti → sodium titanate gel → crystalline sodium titanate gel → porous (top) and dense (bottom) anatase → porous (top) and dense (bottom) rutile. These samples subsequently were soaked in simulated body fluid in order to study the precipitation of hydroxyapatite in the absence and presence of long UV radiation, which has not been investigated before. One sample showed greatly enhanced hydroxyapatite deposition, this being the one oxidised at 400°C, consisting of small amounts of crystalline sodium titanate and anatase, and subjected to UV irradiation. More generally, enhancement of hydroxyapatite precipitation is observed in the presence of anatase and/or sodium titanate; suppression of hydroxyapatite precipitation is observed in the presence of gels and rutile. However, UV light with anatase enhanced precipitation while UV light with rutile suppressed it. This is attributed to the morphological effect of the larger grain of rutile compared to the smaller anatase.

Introduction

Gel oxidation is a thermochemical method used to form a bioactive surface layer on a metallic titanium (Ti) surface. A bioactive layer on the Ti surface is necessary in order to improve tissue compatibility and bonding between the implant and the bone [1]. Gel oxidation is a simple method by which the thickness and morphology of surfaces can be controlled. It can be described in terms of a two-step process:

i) Gelation: Ti metal is treated with a aqueous corrosive reagent, such as NaOH solution, thereby forming a sodium titanate hydrogel [2].

ii) Oxidation: The hydrogel is oxidised at various temperatures, thereby forming a surface layer of recrystallised titania (TiO_2) and possibly other phases, such as sodium titanate, on the surface.

The *in vitro* route to form bone-like hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) coatings on Ti surfaces by immersion in simulated body fluid (SBF) is well established. Kokubo *et al.* [3] have explained that alteration of the surface charge on a sodium titanate surface after immersion in SBF is the first step toward hydroxyapatite formation. Since Ti inevitably is coated with a thin passivating layer of TiO_2, there also have been several studies of hydroxyapatite formation on coatings of this oxide [2,4]. In light of the semiconducting properties of TiO_2 [5], it can be expected that the photocatalytic properties of TiO_2, which are sensitive to UV radiation, and the associated surface electrical phenomena [6] are likely to have a significant effect on the precipitation of hydroxyapatite. Shozui *et al.* [7] subjected rutile coatings on oxidised Ti to UV irradiation *before* soaking in SBF and observed enhanced deposition of bone-like hydroxyapatite. This is difficult to rationalise owing to the fact that the photocatalytic effect is active only *during* irradiation. However, exposure to ambient light during soaking (conditions not specified by the authors) or

possibly sterilisation and/or photocatalysis from ambient UV could explain these results. The present work appears to be the first to report UV irradiation during soaking in SBF (using both anatase and rutile).

Li et al. [8] reported that the most important factor to promote bone-like hydroxyapatite formation on a material in SBF is that the material should have a negatively charged surface in order to attract cations (Ca^{2+} and P^{5+}). Crystalline TiO_2 (especially anatase) is known to be an n-type semiconductor in most circumstances [1,9,10]. When TiO_2 is illuminated by UV light of energy greater than the band gap (E_g), it generates electron-hole pairs, where the electrons tend to reduce Ti^{4+} to Ti^{3+} [1,9,10]. However, the holes tend to be trapped by surface H_2O, yielding $\cdot OH$ radicals [1], which can be assumed to form titanium hydroxide. Hence, the observation by Kasuga et al. [11] that biomimetic formation of hydroxyapatite on TiO_2 is accompanied by the formation of titanium hydroxide groups suggests that the photocatalytic activity of TiO_2 under UV could enhance hydroxyapatite formation. In effect, there are two possible driving forces for this enhancement:

i) Semiconducting: Negative or n-type surface electrical charge and consequent cation attraction
ii) Chemical: Hydroxyl radical presence and consequent hydroxide formation

Experimental Procedure

Sample Preparation. High-purity titanium substrates of dimensions 25 mm × 10 mm × 0.05 mm were wet hand-polished using 1200 grit (~1 μm) abrasive paper, followed by immersion in an ultrasonic bath containing acetone, rinsing with distilled water, and dried with compressed air. NaOH solution of 5 M concentration was used for gelation by dissolving solid NaOH (Univar, >97 wt%) in distilled water.

Gelation. Gelation was performed by soaking each Ti substrate in ~5 mL of solution at 60°C for 24 h in a glass bottle, which was sealed with a plastic cap. The experimental setup, illustrated in Fig. 1, shows that the reaction system was both closed and static. After gelation, the substrates were washed gently with distilled water and dried in air for 24 h. The gelled substrates were placed vertically on an alumina refractory, heated to 400°-800°C (heating rate 300°C/h) in air in an electric furnace, soaked for 1 h, and cooled naturally in the furnace [12].
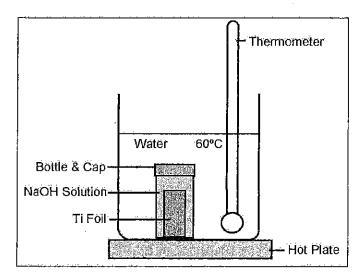

Fig. 1. Schematic of sample preparation in 5 M NaOH solution.

Soaking in Simulated Body Fluid (SBF). The SBF was prepared according to Kokubo's formulation [13] using reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4 \cdot 3H_2O$, $MgCl_2 \cdot 6\ H_2O$, $CaCl_2$, and Na_2SO_4 dissolved in ultrapure water (Milli-Q®), followed by buffering at pH 7.40 with tris(hydroxymethyl)amminomethane ($(CH_2OH)_3CNH_3$) and hydrochloric acid at 36.5°C. The gelled Ti substrates then were sectioned into two specimens (12.5 mm × 10 mm × 0.05 mm). The subsequent treatment was of two types:

i) Without UV: Soaking in 25 mL of SBF at ~37°C for 24 h in a closed chamber (dark)

ii) With UV: Soaking in 25 mL of SBF at 36.5 ± 0.5°C for 24 h during exposure to long-wave UV (TFP-97500-55, wavelength 365 nm, intensity 7 mW/cm^2, Cole-Parmer Corp.) in a closed chamber

In order to maintain a constant SBF temperature, the lamp was set at a distance of 80 mm from the specimen and a radiation cycle of alternating 15 min on and 15 min off was used. The experimental setup is shown in Fig. 2; the same arrangement was used for treatment without UV light. In both types of treatment, the volume of SBF was designed to match that of the total surface area of the specimen [13].
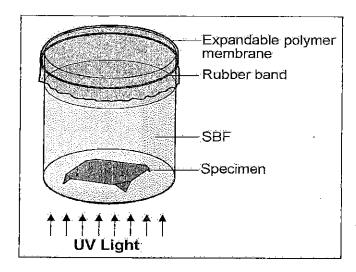

Fig. 2. Schematic of setup for UV irradiation of specimen during soaking in SBF

Characterisation. The mineralogical compositions of the films were determined using glancing angle X-ray diffraction (GAXRD, Philips X'Pert PRO Materials Research Diffraction System) at 45 kV and 40 mA and an angle of incidence of 0.8°. The microstructures were examined using a field emission scanning electron microscope (FESEM, Hitachi, Model S4500 II) at an accelerating voltage of 20 kV. Focused ion beam (FIB, FEI xP200) milling was used for cross-sectional imaging.

Results and Discussion

Gel Oxidation: Fig. 3 shows a modified schematic of the reaction sequence, which consists of five stages, as a function of time, gelation, and oxidation (modified from [14]):
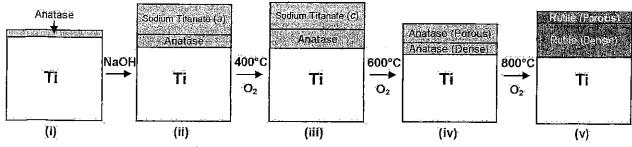

Fig. 3. Schematic of gelation and oxidation

i) A thin passivating layer of TiO$_2$ is present on the Ti substrate owing to ambient oxidation.

ii) During soaking in NaOH, corrosive attack of the TiO$_2$ film and Ti substrate by the hydroxyl groups of the NaOH solution causes dissolution to form an expanded porous network of amorphous (*a*) sodium titanate hydrogel [12,15].

iii) Oxidation at low temperatures (400°C) results in crystallisation of the hydrogel to form crystalline (c) sodium titanate ($Na_2Ti_5O_{11}$) and probably slow further oxidation of the underlying titanium substrate to form anatase, with little dimensional change.

iv) Oxidation at intermediate temperatures (600°C) results in concurrent (1) decomposition of the sodium titanate to volatilise Na_2O and form anatase, (2) probably slow further oxidation of the underlying titanium substrate to form anatase, and (3) densification of the TiO_2.

v) Oxidation at high temperatures (800°C) results in concurrent (1) rapid oxidation of the underlying titanium substrate, (2) phase transformation from anatase to rutile [16], and (3) densification of the rutile. The resultant films, which were of thicknesses ≤ 2 µm, are adhered strongly to the Ti substrates [2].

Fig. 4 and 5 show supporting FESEM micrographs of the surfaces and cross-sections, respectively, in support of the preceding schematic.
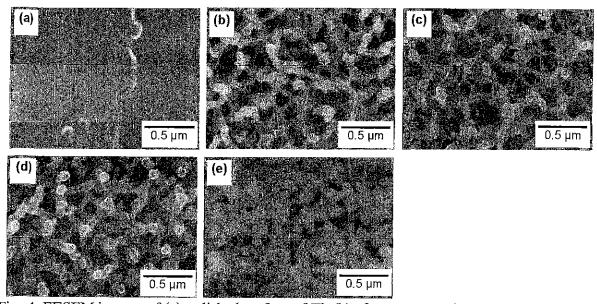

Fig. 4. FESEM images of (a) polished surface of Ti, (b) after treatment in 5 M NaOH at 60°C for 24 h, and after oxidation for 1 h at (c) 400°C, (d) 600°C, and (e) 800°C.

White: Dense
Black: Porous

Size bar is given in two directions owing to 45° viewing angle of the FIB.
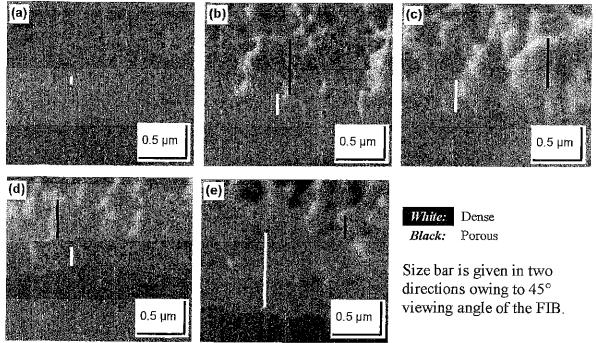
Fig. 5. FIB images of (a) cross-section of Ti, (b) after treatment in 5 M NaOH at 60°C for 24 h, and after oxidation for 1 h at (c) 400°C, (d) 600°C, and (e) 800°C.

Fig. 6 shows the GAXRD data for the surfaces of the substrates as-treated with NaOH and following oxidation at various temperatures. It is likely that the small peaks attributed to sodium titanate ($Na_2Ti_5O_{11}$) after gelation are crystallites deriving from the hydrogel, which has been observed by other researchers [17,18]. It is not clear if anatase (TiO_2) forms during oxidation at 400°C but it is likely to form at 600°C since the obscuring peaks from sodium titanate are absent. Oxidation at 800°C yields only rutile.
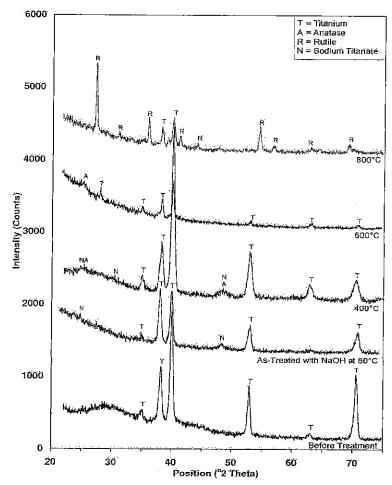

Fig. 6. GAXRD patterns of the surfaces of NaOH-treated Ti subjected to oxidation at various temperatures.

Effect of UV irradiation on hydroxyapatite formation in SBF. Fig. 7 shows FESEM images of the unpolished samples after (a) gelation and oxidation (left column), soaking in SBF for 24 h (middle column), and soaking in SBF under UV irradiation for 24 h (right column). Fig. 8 and 9 show GAXRD patterns for the corresponding samples after soaking in SBF without and with UV irradiation, respectively.

Soaking in SBF without UV irradiation appears to have thickened and smoothed the struts of the network microstructures of the samples as-treated and oxidised at 400°C and 600°C, which suggests the precipitation of a thin layer of hydroxyapatite. Precipitation of very thin layers of hydroxyapatite on gel oxidised Ti has been observed before [19]. The apparent absence of hydroxyapatite in the corresponding GAXRD patterns suggests that, if present, it is below the level of detection of the GAXRD unit. Conclusion about the samples oxidised at 800°C is problematic since the microstructure probably was altered through the grain growth associated with the heating and anatase → rutile phase transformation [20].
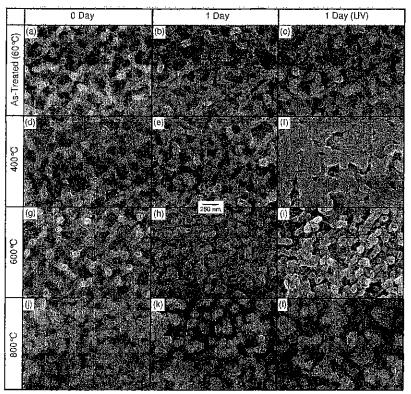
Fig. 7. FESEM images of the unpolished surfaces of Ti substrates treated with NaOH and oxidised at 400°, 600°, and 800°C, followed by soaking in SBF without and with UV irradiation for 24 h.

Fig. 9. GAXRD patterns of the unpolished surfaces of Ti substrates before and after treatment with NaOH and oxidised at 400°, 600°, and 800°C, followed by soaking in SBF with UV irradiation for 24 h.
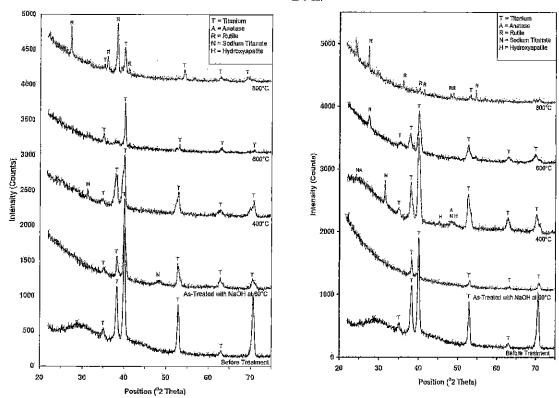
Fig. 8. GAXRD patterns of the unpolished surfaces of Ti substrates before and after treatment with NaOH and oxidised at 400°, 600°, and 800°C, followed by soaking in SBF without UV irradiation for 24 h.

Soaking in SBF with UV irradiation appears to have had a significant effect only on the sample oxidised at 400°C, with considerable precipitation of hydroxypatite and consequent densification. The increased roundness and smoothness of the sample oxidised at 600°C suggests that hydroxyapatite precipitation was enhanced slightly.

The preceding observations allow the following conclusions to be made:

i) Rutile (oxidation at 800°C) has a lower band gap than anatase [6] and so would be expected (for particle sizes and consequent surface areas equivalent to those of anatase) to show a greater photocatalytic effect. However, there does not appear to be any significant enhancement of hydroxyapatite precipitation on rutile.

ii) Anatase (oxidation at 600°C) appears to show only a minor effect on the enhancement of hydroxyapatite precipitation.

iii) However, anatase in the presence of sodium titanate (c) (oxidation at 400°C) shows significant enhancement owing to UV irradiation. The importance of sodium to the precipitation of hydroxyapatite is well known [3].

iv) If anatase oxidised at 600°C does show enhanced hydroxyapatite precipitation, it is likely that residual sodium titanate, below the level of detection of the GAXRD unit, assisted.

Tables 1 and 2 summarise the GAXRD results for the present work other relevant studies. The GAXRD and FESEM data allow the roles of the types and amounts of anatase (A), rutile (R), sodium titanate (NT), and UV light on the precipitation of hydroxyapatite to be elucidated as follows:

Table 1. Observation of hydroxyapatite formation in SBF on the surface of titanium after gelation and oxidation at 400°, 600°, and 800°C.

Oxidation Temperature	Observation of Hydroxyapatite Formation in SBF (Days)				
	Present Work		**Kim et al. [2]**	**Liang et al. [19]**	**Wang et al. [21]**
	SBF	**SBF (UV)**	**SBF**	**SBF**	**SBF**
As-Treated	Not Observed	Not Observed	1	N/A	Not Observed
400°C	1	1	3	N/A	2
600°C	Not Observed	1	3	28*	3
800°C	Not Observed	Not Observed	7	N/A	Not Observed

* Arbitrary time point

Table 2. Minerals and comparative amounts detected by XRD on the surface of titanium after gelation and oxidation of Ti

Oxidation Temperature	**Present Work**	**Kim et al. [2]**	**Liang et al., [19]**	**Wang et al., [21]**
	Solutions			
	5 M NaOH	**5 M NaOH**	**5 M NaOH**	**8.8 M H$_2$O$_2$ + 0.1 M HCl**
As-Treated	NT Gel + NT	NT ≈ R > A	N/A	TiO$_2$ Gel
400°C	NT ≈ A	NT > R > A	N/A	A
600°C	A	NT > R > A	NT	A ≈ R
800°C	R	R > NT	N/A	R

A = Anatase   R = Rutile   NT = Sodium Titanate

A ≥ R   → Enhancement
R > A   → Suppression
Crystalline NT   → Enhancement
Gel   → Suppression
UV Light   → Enhancement

Conclusions

Gel oxidation is a relatively simple method of producing porous but well adhered layers of titania on titanium metal. The oxidation of these layers determines the relative amounts of anatase, rutile, and residual sodium titanate present. Surprisingly, the roles of the different titania polymorphs and sodium titanate appear to be critical to the degree of hydroxyapatite precipitation during soaking in simulated body fluid. That is, anatase and sodium titanate are beneficial while amorphous gels and rutile are deleterious. Surprisingly, it appears that sodium titanate alone may be sufficient to enhance precipitation. More surprisingly, owing to the photocatalytic response of titania to UV light, irradiation with long UV radiation enhanced precipitation with anatase but the effect of rutile was to suppress it. Since the lower band gap of rutile suggests that its photocatalytic effect should be stronger than for anatase, it is concluded that the main difference between the two – the larger grain size of the rutile – is responsible for this result.

Acknowledgements

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