Triple Alkaline Treatment of Titanium Surfaces for Calcium Phosphates Growth

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Titanium surface was chemically modified with sodium hydroxide, sodium silicate and calcium hydroxide with the purpose of improving metal prosthesis to bone adhesion. Results indicate that Ti modified plates immersed in Hanks solution exhibit increased calcium adsorption in comparison to untreated titanium. Calcium silicotitanate, β-tricalcium phosphate and apatites were detected on the coating.

Keywords: Titanium; Calcium phosphates; Titanite; Calcium silicotitanate; Coatings

I. INTRODUCTION

Titanium and its alloys are widely used as biomaterials mainly because of its low density and the outstanding mechanical properties, nevertheless its biointegration falls short from that of calcium phosphates ceramics [1-2]. Obtention of a composite material showing simultaneously the advantages of both, metal and ceramics, has long been sought and has been reached via superficial coatings [3-4].

Perhaps the most known titanium coating process is plasma spray but it has several drawbacks including the use of temperatures as high as 20.000K that negatively affect the phases so deposited converting hydroxypapatite (HA) into tricalcium phosphates and others phases that are more soluble and therefore more easily resorbed [5-6]. Electrodeposition allows for coating preselected phases but it lacks suitable adherence [7].

In this article two methods for the chemical modification of titanium surfaces were conducted for obtaining coatings with chemical and physical properties with closer resemblance of calcium phosphates. This similarity is important for nucleating the above mentioned phosphates on the metal matrix for increased biocompatibility useful in dental and bone implant applications.

The titanium hydrothermal modification with NaOH was undertaken because it creates microrugosity [8] which in the second step, namely sodium silicate treatment, can work as lodging or anchor. The final chemical step purpose is to perform the ionic exchange of calcium for sodium creating a low solubility calcium and silicon containing layer that might induce calcium apatite growth [9-10].The titanium surface hiydrothermal modification with calcium hydroxide has been shown to increase the in Vitro deposition of various calcium phosphates and it was used as a comparison [11-13].

II. MATERIALS AND METHODS

Chemically pure titanium (99.7%) 15x15x0.89 mm plates were cut from foils, sanded with number 600 SiC grit paper in one direction , washed and thoroughly cleaned in acetone with ultrasound and then in acetone in a vapour phase cleaning apparatus for four hours.

For the $Ca(OH)_2$ method used as comparison, freshly cleaned titanium plates were immersed in 0.02M $Ca(OH)_2$aqueous solution at 121 C and 101.300 Pa. (local pressure is 76.642 Pa.) for two hours [11-13]. For the proposed triple alkaline treatment (TAT) also freshly cleaned plates were submerged in 5.0 M NaOH aqueous solution for 24 hours at 95.5C at local pressure and rinsed in distilled water followed by immersion in sodium silicate aqueous solution (Na_2O 8%, SiO_2 27%, density 1.37 kg/L) for 15 minutes, rinsed and finally were treated with 0.02M $Ca(OH)_2$solution for two hours.

The plates so treated were rinsed three times with distilled water and placed in Hanks solution containing the main inorganic electrolytes in concentrations equivalent to those in human blood serum (Table 1) [14] at 37C and pH 7.4 for thirty days with Hanks solution renewal every two days. Plates were then heated at 300C for one hour and blown clean of loose particles with oil free air compressed at 138.000 Pa. through a 1 mm diameter bore nozzle.

Coated plates were characterized by X ray fluorescence (XRF) in a Philips Analytical PW240 apparatus with 2θ ranging from 12° to 147°. Phases composition was studied in a low angle X ray diffractometer (LAXRD) D8 Advanced

Bruker AXS with parallel beam geometry and copper anode (Kα, λ= 1,5405), using incident angle of 2°. Surface morphology and elemental chemical analysis were done by SEM with a Philips XL30 ESEM attached with an EDX system.

TABLE I: Hanks solution molar composition.

Ión	[M]
Na^+	1.45×10^{-1}
K^+	5.82×10^{-3}
Mg^{2+}	8.11×10^{-4}
Ca^{2+}	1.26×10^{-3}
Cl^-	1.45×10^{-1}
HPO_4^{2-}	7.78×10^{-4}
SO_4^{2-}	8.11×10^{-4}
CO_3^{2-}	4.17×10^{-3}

III. RESULTS AND DISCUSSION

Non modified plates surface morphology shows deep parallel sanding scratches that are absent or shallower in treated titanium (Fig.1).

Surface produced by the $Ca(OH)_2$ (Fig. 2), displays crystals of around 10 μm size in which EDAX detected Ca, C, O and Ti indicating the possibility of calcium carbonates, titanates or more complex compounds some of which have been found on titanium under similar conditions [11,12,13].

TAT surfaces (Fig. 3) show aggregates and microcracks, soaking in sodium hydroxide produces the latter solution,

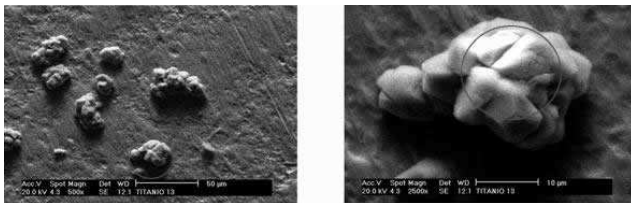(Left)Magnification X 500 (Right) 2500XMagnificación
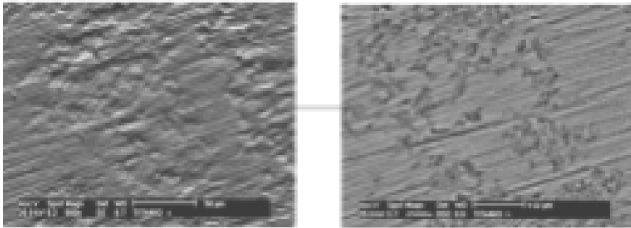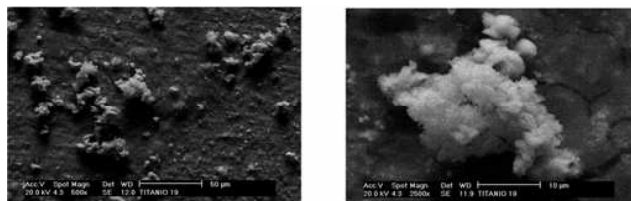

FIG. 1: Unmodified plate.

FIG. 2: Ca(OH)$_2$ treatment plate.

FIG. 3: Triple treatment plate.

result that agrees with those reported by some researchers [8]. These microcracks did not show on Ca(OH)$_2$ or sodium silicate plates (Figs 2, 4 respectively).

XRF results appearing on Table 2 support that Ca(OH)$_2$ plates and those obtained with the TAT have a larger calcium adsorption than that of unmodified metal, indicating that both processes are effective.
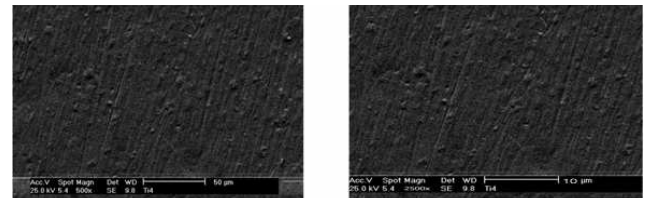
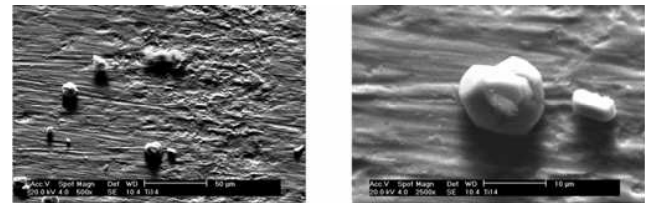

FIG. 4: Sodium silicate modified plate.

FIG. 5: Ca(OH)$_2$plate plus nucleation.

Calcium and phosphorus surface contents after nucleation of TAT plates are larger than the contents of reference treatment plates, observation also supported by micrographs for chemically modified and nucleated plates (Figs. 5 and 6).

Nucleated TAT plates contain less calcium than non-nucleated TAT plates indicating that some calcium dissolution occurs during the month immersion in Hanks solution and that remaining calcium, as well as other elements, are probably irreversibly bond to the surface layer.

EDAX elemental analysis in the circle in Fig. 6 taken on metal surface, not on crystals, indicated Ti, Ca, P, Si, Mg and O suggesting that besides crystals there is a complex layer or a layer mixture of simpler compounds (Fig. 7).

Ca/P ratios calculated from table 2 differ from values expected for biomedical applications calcium phosphate compounds such as hydroxyapatite (stoichiometric HA Ca/P 1.67) and beta tricalcium phosphate (stoichiometric β-TCP Ca/P 1,5). This can be explained in terms of partial substitution of magnesium, sodium, potassium or vacancies for calcium in the case of cations and HPO_4^{-2} or CO_3^{-2} for the anions. These ions originate from the Hanks solution at the given pH except for carbonate that comes also from atmospheric CO_2 that was not excluded from reactions or solutions because natural bone and teeth hard tissues contain carbonates since they are cell synthesized in carbonate containing biological fluids. Other possible causes stem from the formation of salts with other anions during the process namely silicates, titanates and silicotitanates as detected by XRF, EDX and LAXRD.
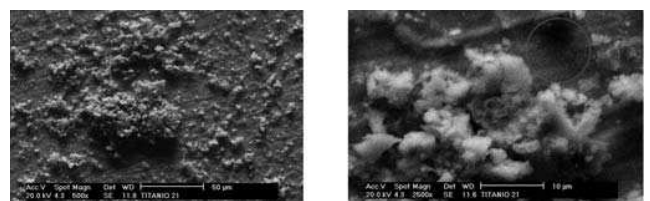

FIG. 6: Triple treatment plates plus nucleation.

TABLE II: XRF coating calcium and phosphorus contents.

Treatment	% Ca	% P	%Mg	%Ca/%P
Ti unmodified	0.088	0.132	0.000	0.667
Ca(OH)$_2$	0.158	0.004	0.047	-
Ca(OH)$_2$/Nucleated	0.108	0.020	0.209	5.40
TAT	0.840	0.042	0.232	-
TAT/Nucleated	0.353	0.212	0.000	1.66

Also Ca/P weight ratios are an average value for the XRF analytical volume that probably are non uniformly distributed but follow a gradient profile originated in the different treatments, nucleation and heating.

LAXRD showed β-TCP and calcium apatites on modified and nucleated plates. TTA plates showed calcium silicotitanate or so called titanite (Fig. 7), results that agree with those of EDX and XRF. Coating on Ca(OH)$_2$ plates contained calcium perovskite (Fig. 8).
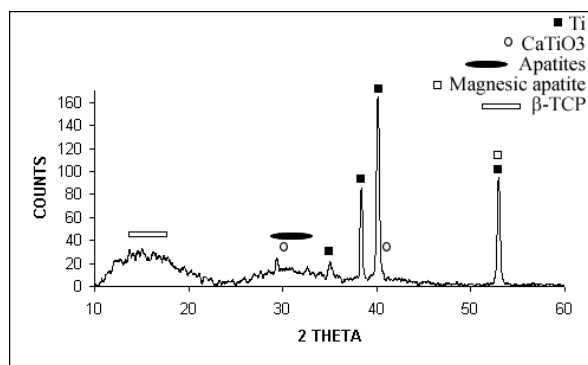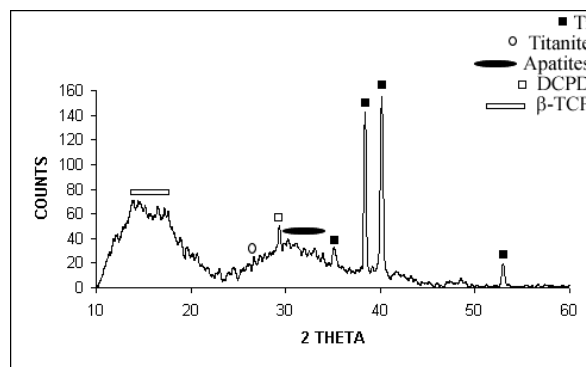

FIG. 8: LAXRD of nucleated Ca(OH)2 plate.

IV. CONCLUSIONS

Titanium plates modified with TAT develop an increased capacity for calcium and phosphate adsorption and nucleation compared to unmodified titanium and also to Ca(OH)$_2$ modified titanium. β-TCP, calcium apatites and titanite are produced on triple alkaline treated titanium surface.

Acknowledgements

FIG. 7: LAXRD of nucleated TAT plate.

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