Sol-gel multilayer hydroxyapatite coating for dental implants osseointegration

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Statement of Purpose: One of the main successful factors related to the use of joint prostheses and osseointegrated dental implants is related to the fixation of the device to the bone. In the last few years CaP sol-gel deposition has been studied and experimented [1, 2]. The low processing temperatures, the possibility to work with complex implant geometries and to obtain thin films make sol-gel a promising technology especially for the coating of osseointegrated dental implants. The purpose of this research was to perform a physico-chemical and biological characterization of a sol-gel thin hydroxyapatite coating deposited on titanium. The deposition has been developed and performed on three different surfaces, characterized by different roughness and morphology, associated to three different surface finishing for dental fixture.

Methods: ISO 5832-2 grade 2 titanium disks (diameter 12 mm, thickness 0.5 mm) were used for the preparation of all samples. Al disks were acid pickled for 120 seconds in a 20% (v/v) of nitric acid with 3% (v/v) of hydrofluoric acid. Three different substrates were considered: A) simple acid pickled finished surface (namely **acid-etching**) as previously described; B) micro-rough surface (namely **BioRough**) obtained by an alkali treatment followed by a proper acid etching [3]; C) macro-rough surface (namely **BioBlast**) obtained by grit blasting process, with 200 μm diameter calcium/magnesium carbonate grits, followed by a nitric acid soaking, used to dissolve the residual calcium/magnesium carbonate grits. A multilayer sol-gel coating topped with hydroxyapatite was obtained through a three stages sol-gel process: 1) TiO_2 coating was firstly obtained from a solution of titanium isopropoxide in ethanol and HCl. Samples were deep coated, then a thermal treatment was performed up to 300°C. 2) After treatment 1, a $CaTiO_3$ film was obtained through deep coating in a solution of $CaNO_3 \cdot 4H_2O$ and titanium isopropoxide in ethanol. Afterwards a thermal treatment was performed up to 450°C. 3) $Ca_{10}(PO_4)_6(OH)_2$ topping film was obtained by deep coating in a solution of $CaNO_3 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ in distilled water. Two hydroxyapatite layers were obtained repeating the dip-coating. 300°C heat treatment was finally performed.

Physico-chemical characterization was performed by XRD, SEM-EDS, ICP-OES, laser profilometry and contact angle measurements. A preliminary biological in vitro characterization was performed using MG-63 (ECACC, 86051601) and L929 (ECACC, 85011425) cell lines. Cell viability was assessed by Alamar Blue test and cell morphology was assessed by SEM observation at different time points.

Results: The coating obtained on all substrate was homogeneous and stable with a thickness around 1 μm. EDS microanalysis detected the presence of Ca and P on the surface of each sol-gel treated sample, then quantified with ICP-OES spectroscopy (Table I).

Table I	***Ca (μg/cm²)***	***P (μg/cm²)***
acid-etching-SolGel	1,75	0,33
BioRough-SolGel	1,66	0,33
BioBlast-SolGel	1,94	0,31

XRD showed the presence of TiO_2, $CaTiO_3$ and hydroxyapatite on all coated samples. The sol-gel film was found to slightly decrease the average roughness Ra, especially for samples BioRough and BioBlast (Figure 1). A similar trend was observed on contact angle measurements (Figure 2).

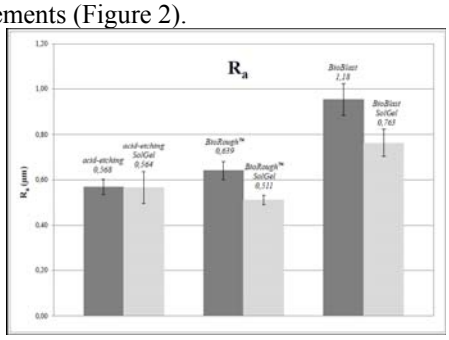

Figure 1. Roughness measurement results

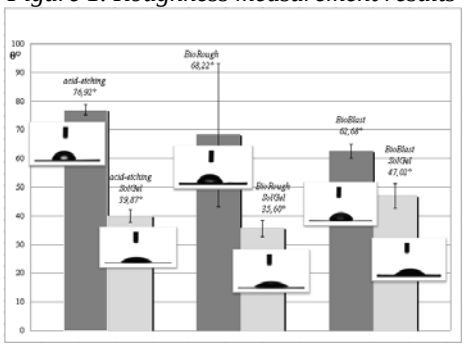

Figure 2. H_2O contact angle measurement results

The Alamar Blue tests on MG63 osteblast-like cells and on L929 murine fibroblasts showed no statistically significant differences ($p > 0,05$) in the level of cellular activity for all the samples analyzed at each time-point.

Conclusions: The temperatures necessary to induce crystallization of the deposited layers, as high as 450°C, avoided any change in the titanium metallographic structure. The obtained multilayer film was found to increase the hydrophilicity of the surfaces and showed no cytotoxic effects on MG-63 and L929 cell line. Althogh extended biological tests are necessary, we believe that this sol-gel process represents a promising alternative for the surface enhancement of osseointegrate micro-roughened titanium surfaces used for dental implant applications.

References: 1) S Un et al.; J Biomed Mater Res B Appl Biomater 90 (2) (2009): 574-583. 2) W Weng et al. ; J Mater Sci: Mater Med 9 (1998):159-163. 3) C Giordano et al.; The Inter J of Artif Org; Vol. 29 no. 8, 2006 pp. 772-780.