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Dental implants electrolytically coated with hydroxyapatite

Implantes odontológicos revestidos eletroliticamente com hidroxiapatita

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Resumo

Esse estudo apresenta um novo método de recobrimento de placas e implantes de titânio com hidroxiapatita, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Foram utilizadas placas de titânio (catodo) comercialmente puro imersas em uma solução eletrolítica rica em íons Ca^{2+} e PO_4^{3-} e um anodo de platina. Foi obtida uma camada de monetita (CaHPO_4), posteriormente convertida em hidroxiapatita através da imersão em uma solução alcalina de NaOH. O processo eletrolítico de recobrimento de implantes dentários foi desenvolvido como alternativa à deposição de hidroxiapatita por "plasma spray", que é a técnica de recobrimento mais utilizada comercialmente. O novo processo, simples e barato, permitiu a obtenção de uma camada homogênea de hidroxiapatita na superfície das chapas de titânio após conversão da monetita em uma solução de NaOH. Observou-se que a conversão de monetita em hidroxiapatita se dá através da reprecipitação de nanocristais de hidroxiapatita a partir de seus precursores, os cristais de monetita. A rugosidade superficial obtida e o fato da hidroxiapatita ser uma cerâmica bioativa pode significar uma redução no tempo necessário à integração osso-implante. Isso é particularmente interessante nos casos em que se empregam implantes endosséus de dois estágios, que são implantes que requerem duas intervenções cirúrgicas.

Palavras-chave: Hidroxiapatita, Implantes dentários, Recobrimento, Titânio.

Abstract

This study presents a new hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) coating method for titanium plates and implants. Titanium plates were used as cathode in a solution rich in ions Ca^{2+} and PO_4^{3-} with a platinum anode. A monetite (CaHPO_4) coating was obtained and then converted to hydroxyapatite by immersion in an alkali NaOH solution. The electrolytic coating process for dental implants was developed as an alternative to hydroxyapatite coating by plasma spray technique. The new process, simple and inexpensive, yielded a homogeneous hydroxyapatite layer on the surface of the implants after conversion from monetite in a NaOH solution. The conversion from monetite to hydroxyapatite occurs by reprecipitation of hydroxyapatite nanocrystals from the precursor monetite crystals. The surface roughness and hydroxyapatite bioactivity obtained can result in a reduction in the necessary time for bone-implant integration. This is particularly interesting for two stage endosseous implants, that are implants that require a two-stage surgery.

Keywords: Coating, Dental Implants, Hydroxyapatite, Titanium.

Introduction

Dental implants comprise endosseous and subperiosteal implants. Subperiosteal implants “embrace” bone, while endosseous – widely used due to their clinical success – are fixed to bone, normally having the shape of plates, blades or screws. This class of implants were specially developed after the introduction of the term osseointegration by Brånemark and co-workers in the 1970’s (Brånemark, 1985). There has been much discussion of the meaning of this term since then and Williams defined osseointegration as being “the concept of a clinically asymptomatic attachment of a biomaterial to bone, under conditions of functional loading.” (Williams, 1999).

Titanium is the most widely used metal for osseointegrated implants. Recent studies have concentrated efforts in improving surface properties to generate a faster bone-implant integration with the aim of reducing the total time between surgeries, when the implantation is done in two stage surgery. In this surgical procedure, a first intervention is done to insert the implant in the bone site. In the second stage, after healing has taken place, the prosthesis, i.e., the artificial tooth and an adapter, is screwed to the implant thus submitting it to load-bearing conditions. The use of bioactive materials coatings a more rapid bone response has been investigated and the most widely used bioactive material for this purpose is hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

The most widely used coating technique is plasma spraying, that consists of accelerating hydroxyapatite particles toward a metallic substrate with the aid of a plasma flame. This process has some disadvantages such as the hydroxyapatite decomposition due to the high temperatures of the process and high costs of equipment acquisition and maintenance. As a result, several techniques of hydroxyapatite coating have been proposed (De Andrade *et al.*, 1998; De Groot *et al.*, 1994; De Groot, 1998; De Moraes *et al.*, 1999; Prado da Silva, 1999). The expression “hydroxyapatite coating” must be used only when one is sure about the calcium phosphate composition. Even with the same coating technique, for example, plasma spray, coatings with varying properties can be obtained, depending on the process parameters.

The biological response of biomaterials is a result of interactions between biomolecules and atoms on the surface (Prado da Silva, 1999). It is thus very important to determine surface properties when designing implants because bone response is strongly dependent on the external atomic layers. Several

characterisation techniques are used including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), which give important data about surface chemistry, whereas scanning electron microscopy (SEM) gives information about surface morphology.

Biological characterisation is generally subdivided into *in vitro* and *in vivo* tests. The two most frequent *in vitro* tests are the tests undertaken in simulated body fluids (SBF), developed by Kokubo *et al.* (1990) and cell culture (Toth *et al.*, 1995). In SBF tests, bioactivity is assessed by the ability of forming apatite *in vitro*. These are qualitative and comparative results, as there are other solutions simulating biologic fluids and there is not a normalisation of those tests concerning the periodic change of the solution. These tests are simple to perform and can in some ways predict the *in vivo* behaviour of the implant.

The present study presents an alternative method of hydroxyapatite coating, conjugating low cost to simplicity. This process consists of an electrolytic deposition of monetite (CaHPO_4) on titanium substrates and its further conversion to hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Prado da Silva *et al.*, 2001A). The resulting coating was characterised by XRD, XPS and SEM and its bioactivity was assessed by SBF tests (Prado da Silva *et al.*, 2001B).

Materials and Methods

The electrolytic method presented in this study consists of the application of a potential difference between a platinum anode and a titanium cathode (plate to be coated). The electrodes are immersed in a solution rich in ions Ca^{2+} and PO_4^{3-} which composition is: 0.5M $\text{Ca}(\text{OH})_2$, 0.3M H_3PO_4 and 1M $\text{CH}_3\text{CHCO}_2\text{HOH}$ (lactic acid). The solution is heated up to 80° C and the coating process is performed by applying a current density of 0.15-0.30 mA/cm² during 50 minutes. Figure 1 presents schematically the electrolytic apparatus.

After deposition, the sample was washed in distilled water and air dried. The conversion from monetite to hydroxyapatite was done in a solution 0,1M NaOH at 60° C during 24 hours. The coating composition was characterised by XRD and the morphology was assessed by SEM. Hydroxyapatite coated specimens were immersed in SBF solution to assess bioactivity. The solution was prepared according to the procedure described by Kokubo *et al.*, 1990) and then observed in SEM.

XRD analysis was performed according to the θ -2 θ method with $\text{Cu}_{K\alpha}$ ($\lambda=0,1542\text{nm}$) at 40kV and 40mA.

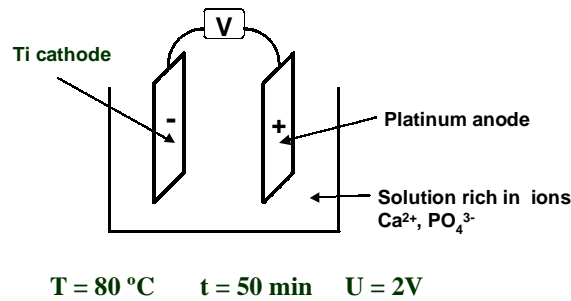


Figure 1. Scheme for monetite coating on titanium substrates.

XPS analysis was performed in a 1257 PHI spectrometer using $\text{Mg}_{\text{K}\alpha}$ operating at 13kV and 54° , with 1253.6eV.

X-ray photoelectron spectroscopy analysis (XPS) was performed in order to assess the chemical purity of the titanium substrate before coating as well as the chemical composition of the produced hydroxyapatite coating.

Results

Figure 2a presents the surface of a commercially pure titanium sheet before coating. SEM analysis revealed the morphology of the monetite crystals, as presented in Figure 2b.

Figure 3 presents the hydroxyapatite coating obtained after alkali conversion from monetite. The microstructure consists of nanocrystals of hydroxyapatite. The XPS analysis on commercially pure titanium implants did not show the presence of any contaminant element, being carbon, oxygen and titanium the only present elements. The XPS analysis on the hydroxyapatite coating revealed the presence of Ca, P, C and O, together with traces of sodium.

Figures 4a and 4b show the XRD patterns of the samples before and after monetite conversion by immersion in NaOH solution. From Figure 4a, it can be observed that the electrolytic process produces a coating that consists in pure monetite. After conversion in alkali solution, the coating is completely converted to pure hydroxyapatite (Figure 4b).

After immersion in SBF solution, an apatite layer was observed. Figure 5 presents the coating morphology after SBF immersion for 3 days.

Discussion and conclusions

Figures 2b and 4a show respectively monetite crystals morphology in SEM and the corresponding XRD pattern. A continuous coating corresponding to

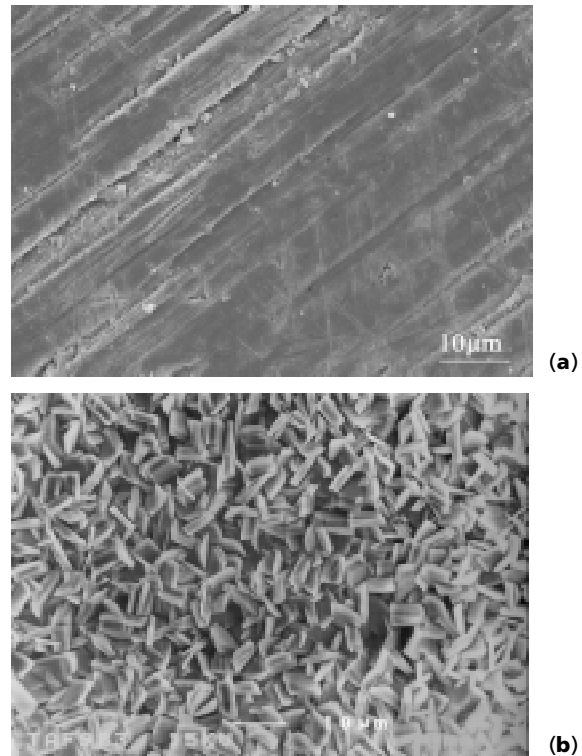


Figure 2. SEM analysis on surface of: (a) commercially pure titanium before coating and (b) commercially pure titanium electrolytically coated with monetite.



Figure 3. Hydroxyapatite morphology assessed by SEM analysis.

parallelepiped-shaped crystals was observed by SEM. This analysis also revealed that the coating was continuous, homogeneously covering the area of the titanium specimens. The dimensions of the monetite crystals were found to be in the range from 2-10 μm . XRD analysis identified this coating as being pure and crystalline monetite, CaHPO_4 with no other calcium phosphate phase detected.

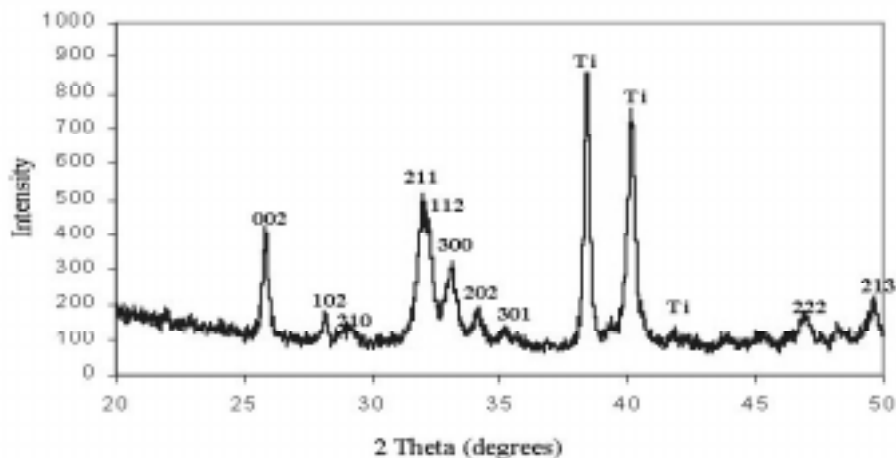


Figure 4. XRD patterns for sample after hydroxyapatite conversion.

Figure 3 shows the coating after the conversion from monetite to hydroxyapatite. The comparison between Figures 2b and 3 indicates that the conversion from monetite to hydroxyapatite in a solution 0.1M NaOH at 60° C during 24h was followed by a morphology change. The former monetite crystals gave rise to hydroxyapatite crystals with dimensions in nanometric scale. This finding is different from what was observed by Redepenning *et al.* (1996), who obtained hydroxyapatite from monetite without morphological change. The XRD pattern shown in Figure 4 indicates the presence of only one phase: hydroxyapatite. The produced hydroxyapatite coating exhibited a preferential growth along the *c* axis, as reported previously (Oliveira *et al.*, 2001), where it is demonstrated that the intensity along [002] is higher than usual. The monetite pattern exhibited a preferential growth along the [112] axis.

The final coating comprised hydroxyapatite nanocrystals arising from former monetite crystals. This morphology of nanocrystals suggests an increase in surface area when compared to the former monetite parallelepiped-like structure. The nanometric dimensions of the hydroxyapatite crystals are in the same range of bone mineral nanocrystals, that are smaller than 100nm. (Toth *et al.*, 1995).

XPS analysis indicated that the final coating corresponds to a calcium phosphate with Ca/P between 1.60 and 1.70. This result is in accordance to

the XRD analysis, which indicated the presence of pure and crystalline hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, that has Ca/P=1.67. In a previous study, Oliveira *et al.* (2001) assessed the transformation from monetite to hydroxyapatite by XRD with structure refinement. In this study, the lattice parameters remained constant for different conversion time points, confirming the coating to be stoichiometric hydroxyapatite. Although the XPS analysis showed a variation from 1.58 to 1.70 on the Ca/P ratio, this variation is within the range of uncertainty of the XPS analysis.

The bioactivity tests showed that the resulting coating is bioactive. Previous studies on the bioactivity of the produced coating indicates that it is highly bioactive, showing the first apatite nuclei after 1 day immersion in SBF (Prado da Silva *et al.*, 2001B). This result of high bioactivity is in apparent contradiction with a stoichiometric and highly crystalline hydroxyapatite coating. One possible explanation for this finding is the high surface area of the nanocrystalline coating. To support this hypothesis, apatite formation have been reported on the surface of titanium activated by chemical processes (Kokubo *et al.*, 1996) and these authors associated this bioactivity not only to the chemical composition of the surfaces, but also to surface topography.

The present process showed to be economically viable and capable of producing bioactive and rough surfaces. Additional tests involving in vivo studies

must be carried out in order to allow industrial application of the coating process.

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