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# Zinc-modified hydroxyapatite coatings obtained from parascholzite alkali conversion



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#### ABSTRACT

In this study, a novel method of zinc-substituted hydroxyapatite coating is presented. The technique consists of a two-step hydrothermal process. In the first step, the coatings consisted of parascholzite (JCPDS-01-086-2372), a mixture of parascholzite and monetite (JCPDS-01-071-1759) or parascholzite and brushite (JCPDS-72-0713), depending on the Zn concentration in the precursor solution. The second step consisted of an alkali conversion in a KOH solution. The resulting coating was identified as zinc-doped hydroxyapatite.

Growing amounts of ZnO were identified for the coatings obtained with higher Zn content. Rietveld refinement revealed a slight decrease in the unit cell volume, due to zinc partial substitution, when compared to pure hydroxyapatite coatings.

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#### 1. Introduction

Metallic biomaterials are used in structural applications such as dental and femur implants. Titanium is the most widely used metal, due to its strength/weight ratio and excellent biocompatibility. Since osseointegration has been defined as a very close contact between the newly formed bone and implant [1], studies have concentrated efforts in improving surface properties to generate faster bone-implant integration with the aim of reducing healing time [1–7]. It is particularly interesting in dental implant surgeries, when the implantation is done in two-stage surgery [8–10]. 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 coatings elicits a more rapid bone response in comparison to conventional metallic prostheses. This finding is due to the chemically bound bone-implant interface. The bioactive material commonly used for this purpose is hydroxyapatite,  $Ca_{10}(PO_4)_6(OH)_2$ , from which bioactivity and osteoconductivity have been intensively studied [11–17]. However, osteoinductivity has been reported and associated to structural and surface features of scaffolds and coatings such as specific area and substituted functional groups [18–21].

The most widely used coating technique is plasma spraying, which consists of accelerating the coating particles towards a metallic substrate with the aid of a plasma flame. This process has some disadvantages such as the coating decomposition due to the high temperatures

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of the process and the high costs of equipment acquisition and maintenance. During the coating process, calcium phosphate phases other than hydroxyapatite may be present, depending on the process parameters [22,23]. Alternative techniques have been proposed [24–34] towards mimicking biological apatites. Among the alternative methods, those low-temperature ones have the advantage of producing resorbable low-crystalline apatites that closely resemble bone-like apatites. Specially designed to mimic biological apatites, carbonate groups are introduced in hydroxyl and phosphate sites during aqueous syntheses.

In previous studies, an alternative method of hydroxyapatite coating on titanium and niobium was developed [24,35,36]. This process consists of an electrolytic deposition of monetite (CaHPO<sub>4</sub>) on titanium substrates and its further conversion to hydroxyapatite  $Ca_{10}(PO4)_6(OH)_2$ . Experimental tests on niobium and titanium surfaces indicated that the presence of electric charged species has an essential role on the monetite nucleation process. Both metals develop OH<sup>-</sup> charges after immersion in the transparent solution used to produce the coatings. The previous electrolytic coating method on titanium substrates was simplified to a purely hydrothermal method. The process thus consists of a two-step method used to coat titanium and niobium substrates [36,37]. In the first step, a monetite coating is deposited on the thin metallic oxide layer of the substrate by precipitation from a solution rich in calcium and phosphate ions. In the second step, the monetite coating is converted to hydroxyapatite by alkali hydrothermal conversion. The resulting coating showed to be highly bioactive and biocompatible [36,38], with the presence of carbonate substitutions and an XRD pattern very similar to the mineral phase of bone.

Although thermodynamically stable hydroxyapatite is predicted after the alkali conversion, kinetics will allow or not allow the presence of thermodynamically stable phases. On dense particles, thickness can



Fig. 1. Monetite (a) and (b) and hydroxyapatite (c) coatings observed by scanning electron microscopy (SEM) showing smooth monetite crystals before conversion to needle-like hydroxyapatite precipitates (c).



Fig. 2. XRD patterns of the monetite coating before conversion.

limit the extent to which conversion reactions will take place [39,40]. For this purpose, incubation in the alkali solution is carried out for 24 h.

Although biocompatible, niobium is considered a bioinert or, at maximum, a bioreactive metal, not being bioactive. Like titanium and tantalum, niobium can be bioactivated by hydrothermal alkali treatments [41–43]. These metals can thus be considered as bioreactive, once they can be turned bioactive after alkali treatments [35]. Sodium alkali treatment converts titanium, tantalum or niobium oxide to sodium titanate, tantalate or niobate salts, respectively. This structural change that occurs on the surface oxide layer provides nucleating sites

for apatite precipitation from simulated body fluid (SBF). Titanium, tantalum and niobium oxides are in the frontier between bioinert and bioactive ceramics, being more reactive than the bioinert oxides from metallic materials used in orthopaedics such as stainless steels, cobalt and cobalt alloys. It was observed that the substrates are affected by the alkali treatment and the presence of bioactive niobate is associated to oxide modifications that occur during the second step of the coating process. The full process not only coats titanium and niobium substrates, but also eventually turns uncoated parts of the substrate bioactive. In fact, tantalum metal is already being used as an implant material



Fig. 3. XRD patterns of the coating after alkali conversion, confirming 100% hydroxyapatite.

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