THIN FILMS OF CALCIUM PHOSPHATE ON TITANIUM DENTAL SCREWS: SOL-GEL ROUTE VERSUS PLASMA SPRAY

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ABSTRACT

A comparative study between hydroxyapatite (HA) coatings produced by two different techniques, plasma spray (PS) and sol-gel route (SG) was carried out. Plasma spray is currently commercially used for coating dental and orthopaedical implant devices. Sol-gel offers an alternative technique for producing bioactive surfaces for improved bone attachment. Scanning electron microscopy (SEM) was used for the surface and cross-sectional morphology analysis, while EDX elemental maps were used to define the boundary in the distribution of Ca and P. To evaluate the bioactivity in vitro, the samples were soaked in Kokubo’s SBF solution for 10 days. The weights of the samples were obtained, before and after soaking, using an electronic balance with an accuracy of ±0.0001 g. This study reveals that the sol-gel technique appears to be a good candidate to replace the plasma spray in many biomedical applications.

KEY WORDS
Hydroxyapatite thin films, Plasma - spray, Sol-gel

1. Introduction

After being introduced in the 1960s by Branemark et al. [1], titanium implants have gradually replaced other metallic biomaterials in applications with high mechanical strength requirements, especially for dental implants. Concurrently, attempts were made to fabricate materials with osteoconductive properties (ability to promote the growth of new bone tissue around the implant). Calcium phosphates (CaP) are a class of materials that clearly show an osteoconductivity [2]. Hydroxyapatite [HA-Ca10(PO4)6(OH)2] belongs to the above cited class of materials and shows a strong resemblance with the mineral phase of bone [Ca10.3 (PO4)6.3 (HPO4, CO3)2.7 (OH,CO3)0.3] [3]. Moreover, has been demonstrated that HA coatings on metallic substrates, offer great improvement in the lifetime extension of the implants [4]. The methods widely applied for the realization of bioceramic coatings on titanium implants are: plasma spray (PS), radio-frequency magnetron sputtering (RF-MS), pulsed laser deposition (PLD), sol-gel deposition route (SG), electrophoretic deposition and hot pressing [5]. Comparative studies between some of these techniques were already reported in literature [6,7]. In this paper we present a comparative study between a chemical (SG) and a physical (PS) deposition technique, in terms of morphology and bioactivity of the settled thin films on titanium dental screws.

2. Materials and methods

Titanium IV (Ti) commercial-grade dental screws were supplied by the company A-Z Implant (San Lazzaro di Savena – Bologna, Italy). Figure 1 shows one of the screws before the deposition of HA thin film. As can be seen the screw underwent a sandblasting treatment in order to improve the attachment of the PS film in the knurled region. The SG process does not require such a treatment of the titanium substrate.

Figure 1. Sandblasted titanium IV commercial-grade dental screw as received from A-Z Implant.

2.1 PS coatings

HA powder with a high purity of 99.9 mass% (Riedel-deHaën, Sigma-Aldrich Group) was used for PS coating. The PS process was carried out at the Department of Chemical Engineering, Materials, Raw Materials and Metallurgy of the University of Rome “La Sapienza”. The
PS implant is a Controlled Atmosphere Plasma Spraying (CAPS) equipment by Sulzer Metco Corp. As previously said prior the PS process the Ti screws were blasted with Al₂O₃ grit to roughen the surface. A F4VB (Sulzer Metco Corp) was used to realize the HA coating. The HA coating was carried out under Ar atmospheric condition. The HA coating thickness is about 120 µm.

2.2 SG coatings

SG method offers a molecular-level mixing of the calcium and phosphorous precursors. The samples were obtained through the dip-coating method, starting from a colloidal suspension of HA at the Department of General and Inorganic Chemistry, Analytic and Physical Chemistry of the University of Parma on the basis of previous SG coating experiences [8]. During the dip-coating method the withdrawal speed was optimized depending on the composition and the viscosity of the solution used. The Ti substrates have been carefully cleaned and dried under laminar flow to avoid the deposition of dust. A preliminary treatment at 400°C for 2 hours allows the complete removal of organics on the surface of the screws. After cooling at room temperature, the dipping operations have been carried out.

In order to increase the adhesion between the HA film and the metallic substrate, the same substrate has been preliminarily coated with titanium oxide and calcium titanate, also from a SG solution. For the preparation of HA films three layers have been deposited. After each deposition the samples have been left for 30 minutes under laminar flow and then thermal treated in a furnace. To avoid the formation of cracks on the surface of the film, due to thermal shock, the samples were cooled down slowly inside the furnace. The HA coating thickness is about 5 µm.

3. Results and discussion

To perform cross-sectional observation, the samples were embedded in acrylic resin. They were, then, polished with a series of water-lubricated SiC papers, followed by diamond paste finish. After this preparation, the samples were analyzed by Scanning Electron Microscope (SEM), as for surface observations. Figure 2 shows the preparation of the samples for cross-sectional analysis.

EDX elemental maps were used to define the boundary in the distribution of Ca and P. To evaluate the bioactivity in vitro, the samples were soaked in Kokubo’s SBF (Simulated Body Fluid) solution for 10 days [9].

3.1 Morphological characterization: PS coating

Figure 3 shows the surface morphology of a HA coating produced by the PS technique, revealing that the coating is basically formed by the superposition of partially molten HA particles, leading to the typical splat-shaped structure [6]. These splats leave abundant interconnecting porosity in between them.

Figure 3. Scanning electron micrograph of the surface of a HA coating produced by PS.

Figure 4-(a) shows the cross-section of the HA coating produced by PS. The inhomogeneous morphology seen in the surface observation is also reflected in the cross-section. As can be seen in this SEM micrograph, the cracks appear at the surface level and along the coating-substrate interface. This explains the need of a sand-blasting before the PS coating process, and the reason for the poor bond strength shown by the PS coatings: the coating is not really adherent to the substrate because the anchorage is purely mechanical. Figure 4-(c) and (d) correspond to EDX elemental colour mapping of the cross-section area shown in Figure 4-(a). As can be seen the surface of the coating is rough even if the element are well distributed without any infiltration in the Ti substrate.

Figure 4. (a) Cross sectional observation of PS-HA coating. EDX elemental colour mapping of the area shown in (b): (c), (d) cyan Ti, yellow Ca, red P.
3.2 Morphological characterization: SG coating

Figure 5 shows the surface morphology of a HA coating produced by the SG technique, revealing a crack free nature. The coated screw exhibits a surface having good homogeneity and large area, indicating the possibility of formation of a wide zone in contact with living tissue.

Figure 5. Scanning electron micrograph of the surface of a HA coating produced by SG.

Figure 6-(a) shows the cross-section of the HA coating produced by SG. The HA coating covers the entire surface of the substrate. A minimum thickness of about 5 µm is estimated for the coating. No interfacial debonding is observable between the coating and the Ti substrate. The cross-section examination reveals no detectable cracks, especially for those through or across the coating layer. Figure 6-(c) and (d) correspond to EDX elemental colour mapping of the cross-section area shown in Figure 6-(a). EDX maps show a well defined boundary in the distribution of Ca and P, limited to the coating and without any infiltration in the Ti substrate, even if it is evident a scattering of HA in the resin, probably due to the setting of the samples during the polishing with a series of water-lubricated SiC papers, followed by diamond paste finish.

Figure 6. (a) Cross-sectional observation of SG-HA coating. EDX elemental colour mapping of the area shown in (b): (c), (d) blue Ti, red P and green Ca.

3.3 Bioactivity tests in SBF solution

The films underwent in vitro evaluations for characterizing the influences of the two coating processes on the bioactivity of the Ti screws. Kokubo’s SBF solution [9] was used to test bioactivity with refreshing the fluid every 24 hours. The weights of the samples before and after soaking were obtained in an electronic balance with an accuracy of ± 0.0001 g. After the immersion in SBF solution, the samples were washed using distilled water in order to leach the salts in case settled on the samples (i.e. NaCl). After the leaching the samples were treated in a drying oven until they reach a uniform mass value, this means that all the soaked water is evaporated. The noticed mass gain is therefore attributable to the deposition of apatite from SBF solution.

As shown in Figure 7 coatings prepared by SG resulted more bioactive, showing higher mass variations after soaking, than those prepared by PS. Coatings prepared by SG are also more bioactive than those prepared by PLD technique (Pulsed Laser Deposition) characterized in a previous work of the authors [10].

![Graph showing mass variations of coated samples after soaking in Kokubo’s SBF solution.]

Figure 7. Mass variations of the coated samples after soaking in Kokubo’s SBF solution.

3. Conclusion

In this study HA films were deposited on Titanium IV commercial-grade dental screws. A comparative study was performed between HA coatings produced by two different techniques, the plasma-spray (PS), currently commercially used for the coating of dental implant devices, and the sol-gel (SG), still under investigation but with enormous possibilities to overcome other coating techniques. The PS technique produces HA coatings which are thick (about 120 µm), brittle and inhomogeneous, resulting in the poor mechanical strength values reported in the literature [6]. The HA coatings prepared by SG showed less thickness (about 5 µm) but were more homogeneous and crack-free. Moreover, there are various benefits connected with SG technique such as perfect compositional control, low temperature of the process, good homogeneity of doped gels and easiness to deposit films on various substrates. Coatings prepared by SG resulted more bioactive, showing higher mass variations after soaking in Kokubo’s SBF solution, than...
those prepared by PS. SG process did not find industrial applications yet, but allowed to obtain homogeneous HA films that guarantees a wide contact surface between the metal implant and the surrounding living tissue. We believe that this novel SG process does provide an alternative method to form a HA phase at lower temperature than existing methods reported in the literature.

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References