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Coating of tricalcium phosphates by flame spray

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Abstract. The metal alloys used for prostheses with high mechanical requirements are bioinerts, it means they have low integration with bone tissue, therefore, bioactive coatings are used in order to improve this integration. Hydroxyapatite is one of the most studied materials for this application with good results, however, sometimes there are problems due to wear or tear of the coating leading prostheses loss. Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, in its different phases shows osteoconductivity and higher solubility than hydroxyapatite, however, few studies have been carried out to determine its behavior as a coating for this type of applications. In this work, a study of the behavior of tricalcium phosphate as a coating on Ti6Al4V substrates obtained by flame spraying was carried out. As raw material were used tricalcium phosphate powders obtained by precipitation from calcium nitrate and ammonium phosphate dihydrogen solution, and subsequent calcination at $1,100^\circ\text{C}$. The Ca/P molar ratio obtained is 1.48 and the only present crystalline phase is beta -tricalcium phosphate. The coatings obtained have alpha tricalcium phosphate as only crystalline phase, they have compact morphology with low porosity and good wettability with the substrate, which is an index of good adhesion and good mechanical behavior. The transformation from beta- to alpha- tricalcium phosphate is product of the high temperatures used in the process, which are higher than $1,125^\circ\text{C}$ where this transformation occurs.

1. Introduction

Calcium phosphates are ceramic materials that have been widely used as bone substitutes due to their biocompatibility, bioactivity, osteoconductivity, non-toxicity and absence of pyrogenic or inflammatory reactions. [1-3]. The most commonly used as bone substitutes are hydroxyapatite (HA) and tricalcium phosphates (TCP) [4].

The metal alloys used as implants in places with mechanical requirements are bioinerts, so they do not reach full adherence with the bone tissue causing early detachments. Coatings with bioactive materials give the surface of metal implants a good interaction with tissues and body fluids, act as a physical barrier against the emission of metal ions from the substrate and, at the same time, favor direct bonding between implants bone [5].

Implants with bioactive coatings must meet very specific requirements to ensure adequate biocompatibility and bioactivity, as well as stable behavior throughout their useful life, for which the coating is required to have good adhesion to substrate and optimum porosity [6]. The structure of the deposited layer mainly affects the dissolution rate, which in turn determines the behavior of the coating.

Very poorly absorbable phases are stable for a long time but have less bone integration, while highly reabsorbable can severely weaken and compromise the functionality of an implant system. In coatings



deposited by thermal spraying, the secondary phases are produced by rapid melting and cooling of the particles and have different dissolution rates in the body fluid or in simulated physiological fluids, which allows them to be classified according to their stability, the HA being much more stable than β -TCP, which in turn is more stable than α -TCP and this is more stable than tetracalcium phosphate, which at the same time is much more stable than amorphous apatite (HA stability $\gg \beta$ -TCP $> \alpha$ -TCP $>$ tetracalcium phosphate \gg amorphous apatite) [7]. Although there are a large number of studies of HA as coatings for metal alloys, few have been performed with TCP, even knowing that they have greater osteoconductivity.

In general, the most commonly used techniques for the deposition of bioactive materials have been plasma spraying and high-speed oxygen fuel (HVOF), in general, low-speed oxyacetylene flame spraying is not widely used for biomaterials. However, the thermal spray to the flame (FS) allows to obtain coatings that meet the conditions of crystallinity, adhesion and porosity that are used in biomedical applications, in addition, it is an affordable, versatile and easy to use technique.

Flame spray allows coatings of a wide range of materials to be obtained, including ceramics with a high melting point. The morphology of the coating obtained by thermal projection by flame depends on several factors, among which are: the morphology and chemical composition of the powders, the composition and preparation of the substrate, the spray distance, the gas ratio (acetylene: oxygen) and the flow of feed powders. When planning the preparation of a coating, the parameters are chosen according to the recommendations of the powder manufacturers, the experience of the experimenter and the result of numerical simulations [8].

For its part, Ti6Al4V it is an alloy widely used in industrial and biomedical applications [9]. In this material, aluminum acts as a stabilizer of the α phase, which hinders its hot formation, while the vanadium is a stabilizer of the β phase, that increases the mechanical resistance of this material when heat treated and undergoes aging. [9-11].

Therefore, in this work it is considered important to determine the behavior of TCP coatings on Ti6Al4V alloys in order to evaluate their functionality in this type of applications, considering that when presenting greater osteoconductivity and intermediate dissolution rates compared to crystalline hydroxyapatite and amorphous apatite may have better integration conditions to bone tissue. In this work, the projection parameters or conditions for obtained the coatings, the morphology, the crystalline phases present and the wettability of coatings with the substrate are evaluated.

2. Metodology

The methodology included the preparation and characterization of powders and coatings.

2.1. Synthesis of powders β -TCP

Synthesis of powder β -TCP was carried out using the technique of precipitation in aqueous medium, in which a $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution (0.6 M) is added on a $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ solution (0.4 M), for a time of 15 minutes in a magnetic stirrer, at room temperature and with pH control between 10 and 10.5 by the addition of ammonium hydroxide. All chemicals used were produced by Panreac (Spain). The synthesis is summarized in the Equation (1).



Once the addition of the calcium nitrate solution was completed, the stirring was maintained for a time of 45 minutes. The product obtained was dried for 24 hours at 70°C and subsequently calcined at 1,000°C. The calcined powders were screened and sorted by size, those selected were those that passed through the 200 < 75 μm sieve and were retained in 325 > 45 μm .

2.2. Obtaining coatings

The coatings were deposited on substrates of Ti6Al4V, which consisted of cylinders of 2.5 cm in diameter and 0.5 cm in height, which were prepared with an abrasive blast of corundum to give them an

anchor roughness, then they were bathed in alcohol with ultrasound to eliminate the corundum and the remaining dirt.

The technique used was FS with oxyacetylene, using a modified Eutalloy® Terodyn 2000 torch. The spray parameters were: an oxidizing atmosphere in the ratio 1:3.2, at a spray distance of 12 cm, a feeding rate powder flow of 10.2 gr/min, 6 preheating passes and 3 spray passes, for which rotojet was not used.

2.3. Characterization of products

The chemical composition of the powders and the substrates was determined by X-ray fluorescence (XRF), for which a device with a Thermo ARL Optim'X WDXRF and energy-dispersive X-ray spectroscopy (EDS) was used. The microstructure of powders and coatings was obtained by X-ray diffraction (XRD), with a PANalytical equipment. The morphology was analyzed from micrographs by scanning electron microscope (SEM), obtained with a JEOL brand microscope. The loss of mass of uncalcined powders was obtained by thermogravimetric analysis (TGA), and the temperatures at which the phase transitions occur were determined by differential scanning calorimetry (DSC), with an equipment setsys evolution SETARAM.

3. Analysis of results

The chemical composition of the calcined powders is summarized in Table 1, where a Ca/P ratio = 1.48 is found, and goes according to what was planned to obtain β -TCP.

Table 1. Chemical composition of the phosphates obtained.

| Oxide | CaO | P ₂ O ₅ | Al ₂ O ₃ | SiO ₂ | Fe ₂ O ₃ | ZrO ₂ | NiO | Cr ₂ O ₃ |
|-------|-------|-------------------------------|--------------------------------|------------------|--------------------------------|------------------|--------|--------------------------------|
| % w/w | 53.63 | 46.28 | 0.0448 | 0.0158 | 0.0127 | 0.0083 | 0.0058 | 0.0055 |

The morphology of the powders is shown in Figure 1. In part (a) the powders are observed before calcination without sifting and with a very wide distribution width as seen in part (d). The morphology of the calcined powders is shown in part (b) where particles of uniform angular shape and size are observed, porous and formed by smaller particles that were joined after calcination. In part (c) an approximation to 2000X is shown where the sintering necks are observed between particles of 3 or 4 μm , part (e) shows the size distribution of the calcined powders after being sieved with an average size of 85 μm . The Table 2 shows the results of the elemental composition of the substrates used to obtain the coatings, by fluorescence of R-X. It is observed that the matrix is titanium with aluminum, vanadium and some traces of iron.

Table 2. Chemical composition of the substrate by fluorescence of R-X.

| Element | Ti | Al | V | Fe |
|---------|------------------|-----------------|-----------------|-----------------|
| Wt% | 88.93 \pm 0.16 | 7.11 \pm 0.13 | 3.58 \pm 0.10 | 0.22 \pm 0.01 |

The diffractograms of the samples after drying at 70°C and the sample after calcination at 1,000°C are shown in Figure 2, (a) and (b) respectively. The product dried at 70°C presents the typical curve of an amorphous calcium phosphate (ACP) with enlarged peaks in the areas corresponding to the hydroxyapatite peaks, as published by Eanes in 1998 [12]. The sample calcined at 1,000°C presents a diffractogram with β -TCP as the only crystalline phase.

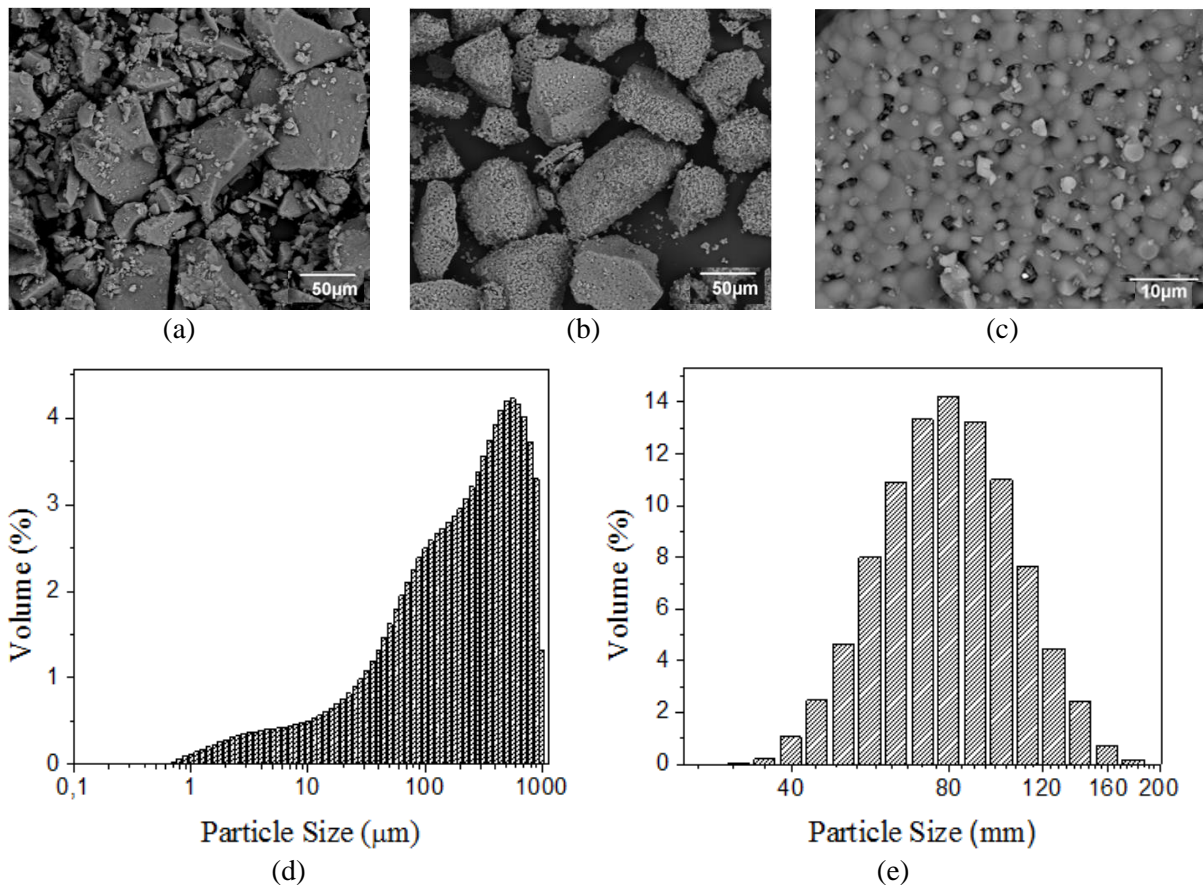


Figure 1. Morphology and size distribution a) and d) of the powders without calcination, b), c) and e) of the calcined powders.

TG curve of the sample without calcination, Figure 3 (a) shows a weight loss of 13% in 4 stages up to 830°C. This behaviour can be explained taking into account the mechanism proposed by Mortier et al. [13] for calcium-deficient hydroxyapatites, $\text{Ca}_{10-z}(\text{HPO}_4)_z(\text{PO}_4)_{6-z} \cdot n\text{H}_2\text{O}$, and that García et al [4] for the specific case of $\text{Ca/P} = 1.5$ when $Z=1$.

DSC curves, Figure 3 (b1) and (b2), show three endothermic peaks. The endothermic peak with a maximum of 750°C that only appears in the sample without calcining (b1), corresponds to the formation of β -TCP. The endothermic peak with maximum at 1,170°C is associated with the transformation of β -TCP to α -TCP, (García, et al) [4], while the peak with maximum at 1,292°C can be associated with the presence of dicalcium phosphate, DCP, in very small amounts not detectable by the XRD technique, as proposed by Destainville [14], and that could be formed in the water loss process of the aforementioned constitution.

The surface and transverse morphology of the coatings is shown in Figure 4 and has the typical characteristics of this technique [8]. In part (a), the splat is observed with a little splash, resulting in a uniform coating with some unmelted particles, which are joined with other completely melted particles. These characteristics are also observed in the same figure in part (b) where the transverse morphology is found, in which well-united porous particles, and interlamellar cracks are observed, as well as the cracks that cross the coatings, that are caused by the residual stress due to thermal shock and which contributes significantly to the porosity of it. The porosity was measured from the SEM image analysis, using the Image J software and gave an approximate value of $32.46 \pm 0.66 \%$. The thickness of the coatings was $190.21 \pm 8.97 \mu\text{m}$. In the same way, a good wettability between the coating and the substrate was observed, which let infer a good adhesion. In part (c) of the same figure the diffractogram corresponding to the coating is shown. It is observed that the only crystalline phase present is α -TCP,

which indicates a total transformation of β -TCP to α -TCP due to the process of heating above the transformation temperature of 1,125°C and rapid cooling of the particles. This reaction corresponds to the endothermic peak found in the DSC, Figure 3 (b2). It is important to note that the dissolution rate of this phase is higher than β -TCP and will therefore have an effect on the osteointegration conditions of the coating.

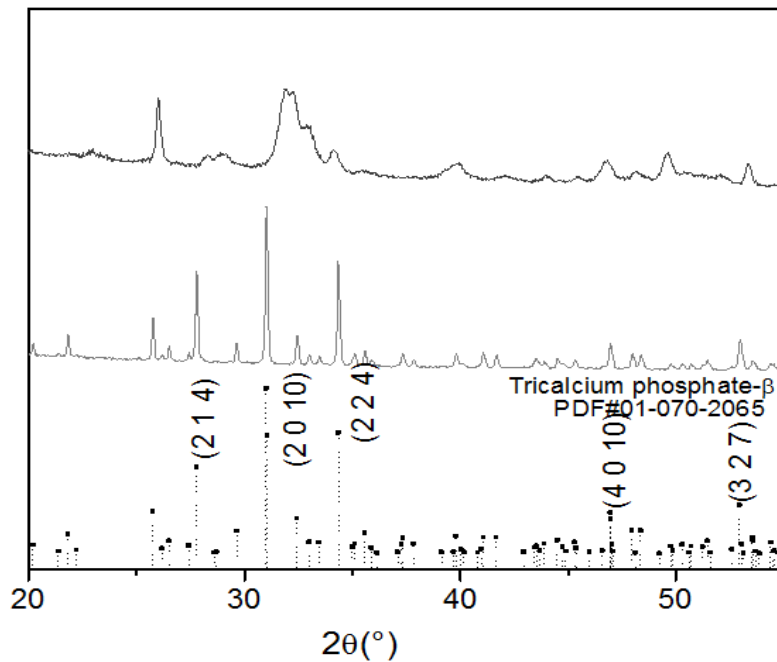


Figure 2. Diffractograms of the calcined and not calcined powder together with the identified pdf.

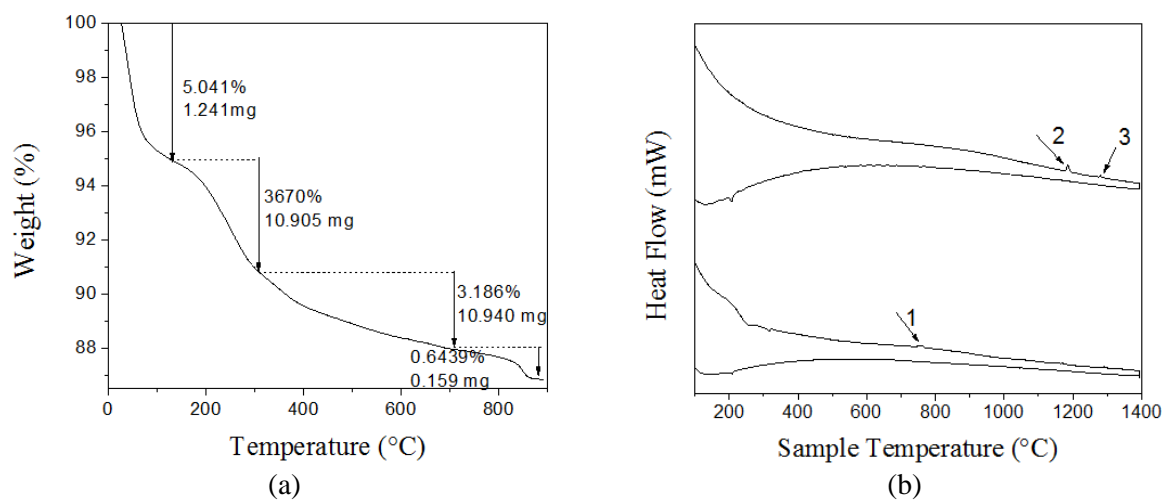


Figure 3. (a) TGA curve for powders without calcining. (b) DSC curves for (b1) powder without calcining and (b2) calcined powder.

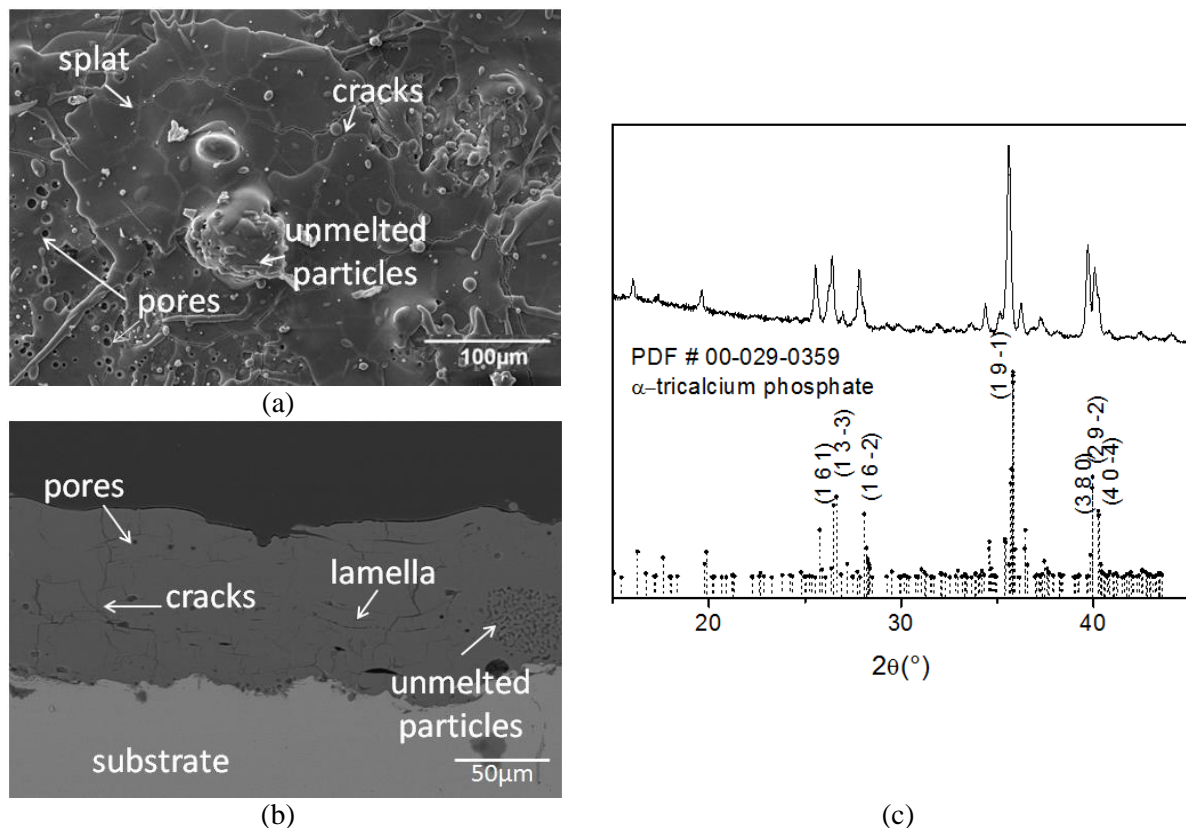


Figure 4. Morphology and microstructure of the coatings. a) Surface section. b) Cross section. c) diffractogram.

4. Conclusions

The coatings obtained have a compact morphology with low porosity and good wettability with the substrate, which indicates good adhesion and makes it possible to assume that they are promising materials for the proposed applications.

Flame spray conditions cause the transformation of the β -TCP phase present in the powders to the α -TCP phase, which means an increase in the dissolution rate of the coating in contact with the body fluids. The method used is simple and allows to produce coatings with composition, mineralogy and controlled densities.

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