Three-dimensional laser-assisted processing of bioceramics

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Abstract

The study of calcium phosphate bioceramics processing by rapid prototyping based on laser cladding was tackled in this work. This technique shows a great potential to provide a three-dimensional tailored implant adapted to the specific problem of each patient. Working window to produce stable geometrical features and repeatable microstructures was established by real time process monitoring and characterization of the processed material. The relationships between the processing parameters and the obtained properties are discussed, in addition to the biological behaviour of the produced parts. The obtained calcium phosphate phases (oxyapatite, tricalcium phosphate, tetracalcium phosphate and amorphous calcium phosphate) are found to favorably influence the degradability of the precursor hydroxyapatite in Tris-HCl buffer which is a good sign of the favorable behavior of this type of materials when implanted “in vivo”.

Keywords: Calcium phosphate; laser cladding; rapid prototyping;

1. Introduction

Bioceramic powders have been used by clinicians in bone disease healing since almost one century ago. Specifically, earliest investigation reports about biomaterials based on calcium phosphate arose fifty years later, in the 1970’s. At the same time, calcium phosphate commercial products were developed and introduced to the market for the first time. Multiple calcium phosphate compounds and composites are nowadays employed in biomedical applications involving bone defect restoration [1].

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Bone implants used in the field of cranial defect restoration must accomplish particular requisites; the desired implant response includes aesthetic functions, tissue protection and support, promotion of bone growth and osseointegration. Between the different ceramic biomaterials, hydroxyapatite (HA), tricalcium phosphate (β-TCP and α-TCP) and tetracalcium phosphate (TTCP) present high bioactivity; thus, these bioceramic materials have been used as bone graft materials for orthopedic and maxillofacial surgery [1-3]. In applications dealing with low loaded implants, like cranial defects restoration, calcium phosphate bioceramic implants fulfill the functional requirements of traditional metallic implants, but also avoid the necessity to be removed from the body. Due to their osseointegration properties, calcium phosphate bioceramics promote new bone growth and the implant integration in the body. However, ceramic materials processing is a delicate task, and a technique to produce bioactive ceramic implants tailored to the patient anatomical parameters is still required.

Cranial defects restoration can be produced by a multi-step process involving the geometrical analysis of the required implant with aid of three-dimensional computer tomography or magnetic resonance techniques. The implant geometry is designed from these data and is translated into information suitable to the rapid prototyping working station. A patient tailored implant is obtained in this way. Different rapid prototyping techniques have been applied to implant production, like stereolithography, laminated object manufacturing, three-dimensional printing and selective laser sintering [5-9]. Nevertheless, many of these techniques are limited to plastic materials and are not able to process ceramic materials. In this work, the rapid prototyping technique based on laser cladding was applied to calcium phosphate bioceramics processing. Optimization of processing parameters to achieve sound grafts and the bioactive response “in vitro” have been carried out.

2. Materials and methods

2.1. Rapid prototyping based on laser cladding

The powder feeding technique was applied to obtain the parts by laser surface cladding [10]. This technique consists basically in blowing particles of the precursor material by a carrier gas over the substrate that is moving across this powder flow and the laser beam (Fig. 1). A stationary high power laser radiation is directed to the surface of the substrate. The laser beam heats up the precursor material cloud and creates a molten-pool on the substrate where the particles impinge. To avoid the oxidation in the interaction zone, a shielding inert gas is applied. Solidification takes place when the molten-pool goes away from the laser irradiated area; thus, a solidified material strip is formed over the initial substrate. A layered part is built when superposing several strips.
The laser source was a Nd:YAG laser ($\lambda = 1064$ nm) with a maximum power of 4000 W (TRUMPF HL 4006D). The laser radiation was guided by means of a 600 $\mu$m core diameter fibre and coupled to the working station via expanding and collimating optics; following, the laser beam was focused over the substrate surface, giving a beam spot with diameter of 2 mm at the substrate upper surface. The focusing optics was a cemented doublet of 250 mm focal length. During processing, a coaxial camera was used to monitor the stability and evolution of the melting pool along the deposited layers. In addition, the average temperature of the laser-material interaction area was remotely measured by means of a pyrometer. This measurement is considered as a preliminary value, owing to the fact that changeable emissivity conditions around the interaction area difficult the determination of precise material temperature values. In addition, for most of the processing parameters explored the area of temperature measurement is more extensive than the melting pool, therefore the values are lower than the real temperature.

The hydroxyapatite precursor powder was fed by a Plasma-Technik powder feeder (model Twin-system 10-C) and injected in the interaction zone by means of a coaxial gas-solid injector. Argon was used as conveying gas and protective gas. Values between 3.5 and 20.5 mg/s were tested for the mass flow, with a carrying gas volumetric flow of 8.0 l/min and a protective inert gas volumetric flow of 16 l/min. During the experimentation the working head, including the focusing optics and the powder injection system, was moved in the vertical direction (z axis), whereas the substrate was moved in a horizontal plane (x and y axis), the three axes where integrated in a CNC station.

2.2. Precursor material

The powder used as precursor material was CAPTAL 90 type calcium hydroxyapatite from Plasma-Biotal UK. The hydroxyapatite crystallinity was above 97.5 %, determined by XRD. Ti6Al4V plates with a thickness of 3 mm and dimensions of 100x150 mm$^2$ were used as substrates.

2.3. Physico-chemical characterization

The obtained samples were geometrically characterized by means of a stereoscopic microscope equipped with an XY positioning stage (Nikon SMZ-10A). The samples microstructure and elemental composition was examined via scanning electron microscopy (SEM Philips XL-30) and an energy dispersive X-ray spectroscopy coupled to the microscope (EDS EDAX PV9760). Chemical composition and crystallinity was determined by means of X-ray fluorescence (Siemens SRS 3000) and X-ray diffraction spectroscopy (Siemens D-5000), respectively. Fourier transform infrared spectra of the overall samples were acquired between 400 and 4000 cm$^{-1}$ with a Thermo Nicolet 6700 spectrometer. To examine structural differences within the sample a Continuum IR microscope coupled to the spectrometer was used to collect the reflectance FT-IR spectra between 650 and 4000 cm$^{-1}$, scanning 100 x 100 $\mu$m$^2$ areas along the sample surface and cross-section.

2.4. Dissolution tests in Tris-HCl buffer

Calcium phosphate samples processed by rapid prototyping based on laser cladding were placed in separate plastic containers with 150 mL of 0.05 M Tris-HCl buffer (Tris(hydroxyl)methyl-aminomethane-HCl), pH = 7.4 at 36.5°C. Immersed samples and solution were kept at 36.5 °C under stirring. At each of the following time periods,
one 6 ml aliquot of solution was taken: 0.5, 1, 3, 6, 10, 24, 48, 72, 168, 336 and 504 h. Control samples of only 0.05 M Tris-HCl buffer were used to discard any influence of the test process in the final results. In addition, precursor HA cold pressed samples with the same dimensions as the laser processed samples were tested for comparison purposes. Three replicas of each different material were tested. Each solution was filtered through sterile filters to remove solids from the liquid and centrifuged to ensure separation of any residual solid. Spectroscopic elemental analyses were performed with inductively coupled plasma optical emission spectroscopy (Perkin Elmer Optima 4300 DV). Calibration for Ca and P analysis were performed with 10 mg/L standards with RSD values below 2.0%.

3. Results and discussion.

3.1. Processing parameters

The working window to produce walls by stacking layers was explored during experimentation. The data acquired by the coaxial camera clearly show the presence of liquid material, demonstrating that the material is not only subjected to sintering transformations. Fluidized material convection is observed within the melting pool; this fact anticipates that hydroxyapatite decomposition is produced during processing. Further analysis of the melting pool by high speed video acquisition from a lateral point of view has shown that biphasic solid-liquid flow is produced at the interaction area. The injected hydroxyapatite particles are still in solid state when impinging on the melting pool and, subsequently, are incorporated into the convective viscous flow of the molten material. Therefore, a possible multiphase microstructure consisting of apatite derived calcium phosphate phases by heat treatment in coexistence with non decomposed apatite is supported by real time observations.

Fluctuations in the size and the shape of the melting pool, along with the measured interaction area temperature, allow to identify the processing parameters settings that produce an stable melting pool and repeatable geometrical and microstructural results. Increasing the process scanning speed leads to a linear size decrease of the melting pool, while modifications of the precursor material mass flow have low influence on the melting pool size. Nevertheless, both high values of the scanning speed and the mass flow produce unstable melting pool, characterized by size and shape variability (see Figure 2), in conjunction with alternating melting pool extinction and resuscitation. The average temperature data of the laser-material interaction area reveals that the lowest temperature values are produced in the conditions of unstable melting pool. The reported behaviour is attributed to interaction area temperatures close to hydroxyapatite decomposition temperature [2, 3].

![Fig. 2. Video captions of the melting pool obtained coaxially to the laser beam: (a) scanning speed 3.5 mm/s, mass flow 9 mg/s, (b) speed 5.0 mm/s, mass flow 15 mg/s.](image)

Correlation of the deposited calcium phosphate layer thickness with the precursor material mass flow and the process scanning speed is shown in Figure 3. At low material injection rates the measured temperature maintains
invariable. Nevertheless, at high mass flow values important temperature reduction is produced due to an excess of injected precursor material in the interaction area. As a consequence, the deposited layers thickness is increased by increasing mass flow rates, but reaches a maximum and stops to increase at high mass flow rates. Similarly, reduction of the interaction area temperature by scanning speed increments is produced as a result of the reduction of absorbed laser energy per part length unit. Therefore, the deposited layers thickness and the obtained part width are in addition reduced by increasing the processing speed.

![Fig. 3. Evolution of the deposited calcium phosphate layer thickness as a function of the precursor material mass flow and the process scanning speed: (a) scanning speed 1.7 mm/s, laser power 150 W, (b) mass flow 13.5 mg/s, laser power 150 W.](image1)

Figure 4 shows the thermal evolution of a representative point in the processed sample for two different parameters settings: processing conditions with an associated excessive cooling rate that leads to sample cracking (Figure 4a), and optimized processing conditions with reduced cooling rates that allow to produce sound three-dimensional samples (Figure 4b). As a result of the cooling-off speeds estimation for the explored range of parameters, it was observed that moderated thermal gradients in proximity of the solidification and phase transformation temperatures produces more beneficial effects compared to reduction of the cooling speed at interaction area temperatures below 1000-900 °C. Phase transformation during cooling and remnant hydroxyapatite decomposition are critical events while processing due to thermal expansion coefficient modification and atoms rearrangement that can actuate as fracture promoters.

![Fig. 4. Interaction area temperature record obtained with to different settings of the processing parameters and the appearance of the respective produced sample: (a) excessive cooling-off speed, (b) moderate cooling-off speed.](image2)
3.2. Composition and microstructure

Scanning electron microscopy images obtained from the samples surface and cross-section are displayed in Figure 5. The surface of the processed samples is homogeneous and shows grains predominantly oriented in the sample growth direction. The XRD diffractograms reveal presence of tetracalcium phosphate (TTCP) and tricalcium phosphate (α-TCP) as the main phases present at the surface. The observed preferential growth is expressed in the diffractogram as a very intense peak in the TTCP pattern.

SEM examination of samples cross-section reveals the presence of different phases as shown in figure 5.b. The backscattered electron micrographs allow to distinguish brighter grains with irregular shapes and more rounded gray grains, both dispersed over a dark grey matrix. The morphology of the irregular brighter grains suggests that incomplete melting of the precursor material has taken place. The EDS analysis shows a homogeneous global elemental composition along the samples complete cross-section, with a Ca/P ratio similar to that of the HA. Nevertheless, the microanalyses of each observed phase performed at different zones of the samples cross-section reveals that the average Ca/P ratio is higher than 1.67 at the rounded gray grains and lower at the matrix. The measured composition of each phase and its Ca/P ratio suggest that the microstructure corresponds to a TTCP dispersed grains in an α-TCP matrix, with the presence of remainder HA irregular grains (see figure 5).

![Fig. 5. Secondary and backscattered electrons SEM micrographs acquired at (a) the surface of a processed sample, and (b) sample cross-section showing the presence of three different calcium phosphate phases.](image)

The XRD analysis of the material processed by laser cladding (not shown), performed after pulverization of the complete samples, reveals the presence of HA, α-TCP and TTCP crystals. In addition, a broad band is observed, indicating that amorphous calcium phosphate is present in the processed samples. The last phase is attributed to an amorphous calcium phosphate phase having the same stoichiometry than HA. This phase, denominated HA glass, was already reported in laser cladding coatings of similar precursor HA material on Ti6Al4V substrates [11-13]. β-TCP, which is the tricalcium phosphate phase stable at room temperature, was not detected in the XRD patterns. Therefore, the cool-off speeds produced during processing prevent the transformation of the metastable phase α-TCP to β-TCP, produced at 1125°C in very low cooling conditions.

Pulverized samples were analyzed by FT-IR and compared to HA precursor material spectrum. Main observed changes are splitting of the antisymmetric stretching vibrational modes of the PO₄³⁻ group, which is characteristic of HA decomposition in TTCP and TCP [14]. In addition, presence of OH groups is not observed in the processed material spectrum; indicating that dehydroxylation has been produced during laser processing. Therefore, the indications of HA presence in the XRD diffractogram must be attributed to oxyapatite presence. Oxyapatite is produced from HA at high temperature previous to decomposition and its diffraction pattern is very similar to that of HA [15]. According to phase diagrams, HA decomposes completely in tetracalcium phosphate (TTCP) and tricalcium phosphate (α-TCP) at 1550 ºC; this phase mixture starts to melt at 1578 ºC. During cooling, the produced CaO-P₂O₅ molten material with the Ca/P ratio of HA solidifies in the α-TCP and TTCP mentioned phases. TTCP is stable at room temperature; nevertheless, α-TCP is a metastable phase transforming in β-TCP at 1125°C. When

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water vapor is not present, HA is not produced during cooling. The cited temperatures are valid for very slow heating and cooling rate values; in the case of laser processing the heating and cooling speed are prominently increased and lead to transformation delays in temperature. Furthermore, transformation of the metastable phase \( \alpha \)-TCP to \( \beta \)-TCP is not produced during processing, and processed samples retain the observed crystallographic structure for years when preserved in standard desiccator conditions.

3.3. Solubility in Tris-HCl buffer.

Processed samples induced \( \text{Ca}^{2+} \) concentration as a function of immersion time in 0.05 M Tris-HCl buffer is shown in Figure 6. At times over 24 h calcium phosphate samples processed by rapid prototyping based on laser cladding showed notably higher \( \text{Ca}^{2+} \) release than that observed for HA precursor material. After 336 hours the concentration is stabilized at approximately 47 mg/L, while the HA leads to an approximated value of 20 mg/L. Furthermore, HA induced calcium concentration at extended times agrees with reported dissolution of similar HA material and different clinically approved commercial HA [16, 17].

Apatite precipitation indications are observed in the phosphorous concentration plot versus reaction time in 0.05 M Tris-HCl buffer, see Figure 7. Modification of the initial phosphorous dissolution rate is reflected by the change of initial curve slope at low values of immersion time. This slope change is observed at approximately 72 h for processed calcium phosphate samples. In addition, release of phosphate due to sample dissolution is counterbalanced by surface incorporation of phosphate from the solution during the precipitation of apatite in the samples surface [3].

The in-vitro solubility of amorphous calcium phosphate, \( \alpha \)-TCP and TTCP is reported to be higher than HA solubility [1, 3, 18]; therefore, the observed ion release in Tris-HCl buffer is in agreement with the calcium phosphate phases distribution observed at the sample cross-sections. In-vivo resorption of calcium phosphate is not only the result of solubility since cell-mediated processes plays a capital role; nevertheless, the implanted bioactive ceramics enhancement effect of bone tissue growth is more boosted for higher solubility rates. The influence of released calcium and inorganic phosphates on bone formation and biodegradation has been suggested by several authors [18-20]. In addition, low-crystalline HA obtained by amorphous calcium phosphate precipitation, alpha-TCP and TTCP is reported to be resorbable calcium phosphate phases, and new bone growth in place of resorbed material was observed when implanted in-vivo [21]. Therefore, mixture of \( \alpha \)-TCP, TTCP phases with hydroxyapatite, which is the case of the calcium phosphate samples processed by rapid prototyping based on laser cladding, is expected to increase the low resorbability of hydroxyapatite.

Fig. 6. \( \text{Ca}^{2+} \) concentration plot in Tris-HCl buffer at early and extended immersion times.
4. Conclusions

In this study the feasibility of rapid prototyping based on laser cladding for processing three-dimensional bioceramic structures was demonstrated. Scanning speed and precursor material mass flow have high influence on the melting pool temperature and are parameters governing the geometrical and microstructural stability of the processed parts.

The microstructure obtained after laser processing is a combination of α-tricalcium phosphate, tetracalcium phosphate and amorphous calcium phosphate phases in coexistence with remaining oxyapatite. This microstructure increased remarkably the dissolution rate of precursor crystalline hydroxyapatite in Tris-HCl buffer.

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