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Surface design using laser technology for Ti6Al4V-hydroxyapatite implants

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HIGHLIGHTS

- New implant surface functionalization: Ti6Al4V laser machining & HAP laser sintering.
- The HAP laser sintering inside the machined spots was optimized using a CO_2 laser.
- Laser technology was proven effective for producing Ti6Al4V-hydroxyapatite implants.
- An effective retention and non-degradation of hydroxyapatite was achieved.
- Validating this design for the production of implants with improved bioactivity.

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ABSTRACT

Although hydroxyapatite coatings have been proven effective for obtaining uniform and continuous coatings on metallic endosseous implants, the detachment of these coatings during implantation can critically compromise the hydroxyapatite bioactive role. In order to overcome this problem, this work proposes a new integrated approach, starting with the laser machining of the Ti6Al4V implant, followed by the allocation of the hydroxyapatite and its subsequent laser sintering. In this study two different powder compaction/laser sintering methods were tested. Hydroxyapatite sinterability and adhesion to the metal was assessed for both methods, considering several conditions. Hydroxyapatite possible degradation due to the temperatures achieved during this process was also evaluated by means of Energy Dispersive Spectrometry (EDS) and X-ray diffraction (XRD). The better solution assured a significant retained volume of non-degraded hydroxyapatite. This work proves that laser technology is a promising approach for the manufacturing of implants with improved bioactivity sites that can overcome the detachment problems of coating-based solutions.

1. Introduction

In dental and other endosseous implants the osseointegration process is a key aspect, dictating the healing time and the implant long-term success [1–3]. Osseointegration and cell attachment to the metal surface and consequent bone formation around the implant are known to be influenced by several factors like the surgical procedure, health and bone quality, the loading upon implantation, the implant design and especially the implant surface [4]. In fact, many studies identify implant surface properties as crucial for obtaining an effective implant-tissue interaction and osseointegration [5,6].

Worldwide, researchers and implants manufacturers are working towards osteointegration improvement, by frequently presenting new solutions, mainly differing on their surface modification [7–12], regarding their topography, chemical composition, the presence of oxides, the surface energy, etc. [13–16]. These modifications can be divided in two main groups: non-porous surfaces (where a suited roughness is promoted [17]) and porous surfaces (not as common as the previous) [18].

Ti6Al4V alloy has been widely used in implants, mainly due to a high chemical stability, mechanical properties and biocompatibility [7]. Several approaches have been used to modify the surface topography of titanium parts [4], towards their application in dental, hip or other types of implants, specifically machining, acid etching [8], sandblasting [7], and laser treatment [9].

Additionally, these surfaces can be coated with bioactive materials like hydroxyapatite (HAP) or other calcium phosphates that are known to stimulate bone growth [19] in order to increase the cell attachment to the metal implant surface [18]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is a calcium phosphate found in teeth and bones [10,20], having an atomic ratio between calcium and phosphorus of nearly 1.67 [21]. Particular attention must be given to HAP condition after processing

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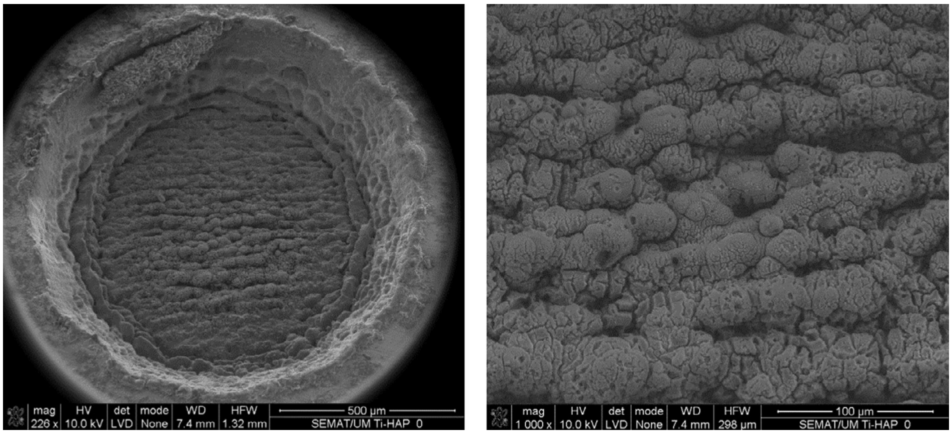

Fig. 1. Laser-generated holes on Ti6Al4V plates.

Table 1
Hydroxyapatite powder specifications.

Phase purity, $Ca_{10}(PO_4)_6(OH)_2$	100%
Particle size, d_{50}, µm	10.0 ± 2.0
Specific gravity, g/cm^3	0.60 ± 0.10

(sintering), once imbalances in Ca/P ratio can indicate the formation of other phases (tricalcium phosphate, tetracalcium phosphate, calcium oxide [22,23]), that will present distinct degradation and solubility rates, affecting the biological response to this material [23–25]. Although presenting a high bioactivity, the low mechanical properties of HAP hamper its use as structural material. In this sense, the most common approach is to apply HAP as coating on a metallic implant [20], although there are some works focusing on the use of HAP as reinforcement in bioactive metal matrix composites [26,27]. Regarding bioactive coatings for dental implants, sol-gel is the most common procedure [20,28], while hydroxyapatite is the most used bioactive material since hydroxyapatite has been proven to be similar to human bone, biologically compatible and to stimulate bone ingrowth, thus adequate for use in dental implants [29,30]. However, although hydroxyapatite sol–gel coatings (e.g. by dip coating) are proven to be adequate for obtaining high-quality coatings on metal substrates [28,30], when used in implants, due to the implantation process, the applied stresses can overcome the coating-substrate adhesion strength and these coatings can be detached from the metal surface, thus compromising their function of promoting osteointegration. The design of surface topographies that could avoid this scenario would be a major breakthrough.

The creation of an implant (dental, hip or other load-bearing implant) having an outer Ti6Al4V-HAP bioactive region that stimulates the surrounding bone tissue, while assuring the bioactive integrity upon implantation would be extremely advantageous.

By laser technology it is possible to produce a designed machined surface, with specific locations where the bioactive material can be allocated. Subsequently, laser can be used to consolidate HAP powders, by sintering them in these designated locations. When selecting a laser for machining or sintering, a match between its wavelength and the absorption characteristics of the corresponding material must be assured for obtaining better results. In this sense, while continuous wave CO_2 laser, with a wavelength of 10640 nm is particularly appropriate for processing ceramics, continuous wave Nd:YAG, having a wavelength of 1064 nm, is usually used on metals [31]. Few studies found in literature show the enormous versatility of laser technology to produce a variety of grooves, holes, patterns and also to laser sinter bioactive ceramics inside these locations [32].

This work presents a new approach for the production of Ti6Al4V doped hydroxyapatite structures for implants applications, by using laser technology, which is sequentially used for the patterning/machining process of the metal substrate and for the sintering of the hydroxyapatite powders. The HAP adhesion to the Ti6Al4V substrate, the HAP sintering and its condition after the laser passage were evaluated.

2. Materials and methods

A Nd:YAG laser was used to produce blind-holes of 1 mm diameter and 0.3 mm depth in Ti6Al4V plates of 3 mm thickness. Fig. 1 shows the holes produced and the roughness obtained by this process.

HAP powder (nanoXIM Hap400, purchased from *Fluidinova)* was dispersed in acetone and used to fill the laser-generated holes. Some specifications of the HAP powder (according to the manufacturer) are presented in Table 1 and images of the HAP powder are found in Fig. 2.

The HAP powder mixed with acetone was afterwards compacted into the holes using a metallic punch with a similar diameter.

Continuous mode CO_2 laser, with a wavelength of 10.5 µm and laser power ranging from 16 to 40 W (see details in Tables 2 and 3) was used to sinter the HAP powders. A scanning line spacing of 0.02 mm was used for all the experiments. Different laser powers were tested, together with a laser speed of 40 or 20 mm/s (Table 2). Fig. 3 schematically illustrates the experimental procedure abovementioned.

Two sets of experiments were performed, using two different powder compaction/laser sintering methodologies.

The first method (hereafter called single-passage method) used one simple compaction step, where the holes were filled completely with HAP, and afterwards a single-passage of the laser performed the sintering of the HAP powder. Table 2 shows the set of experiments that were performed using the abovementioned method (single compaction and single laser passage).

The second method (hereafter called four-passage method) used four times round of HAP compaction followed by laser passage. In each round, the holes were completely filled with HAP with the help of a cylindrical punch.

By this method, HAP is sintered and afterwards new HAP powder is inserted in the holes, being then this new powder layer sintered by the laser. Table 2 shows the set of experiments that were performed using the abovementioned method (four rounds of compaction and laser passage).

Scanning Electron Microscopy (SEM) /Energy Dispersive Spectrometer (EDS) were used to assess the sinterability and adhesion (to the metal) of HAP by using these experimental conditions and also the HAP molar Ca/P ratio after sintering, in order to conclude on their degradation.

HAP phase composition after laser sintering was evaluated by means of EDS and also XRD (D8 Discover, Bruker, Germany) using CuKa radiation (k = 1.5418 Å).