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Mechanical behaviour of dental implants manufactured from metallic powders by µMIM

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Abstract

The micro metal injection moulding (µMIM) is suitable for producing high series of net shaped parts at competitive cost compared with subtractive processes, as dental implants. The µMIM has five main steps: selection of powders and binder, production of feedstocks (mixing), injection moulding, debinding and sintering. The material selected was the 316L steel due to its wide use as biomaterial associated to low cost of powders and its high injectability. The dental implants after sintering have a good finishing, and when coated with thin films enhance osseointegration, and their performance can be superior to the commercial implants. The dental implants were coated with hydroxyapatite to improve the bioactivity. The density, porosity, shrinkage and microstructure of dental implants were evaluated, as well as the mechanical properties like hardness, Young's modulus and torque resistance evaluated in a bovine rib. The new strategic production leads cheaper implants, called "implants for crisis", where surface modification assures a similar or superior bioactivity than commercial implants.

Keywords: microinjection moulding; 316L powders; dental implants; bioactive coatings.

1. Introduction

In the modern society, the longevity of the population is continuously increasing and naturally requirements of dental substitution. Solutions are needed to overcome this problem. Dental implants existed for many years and they include artificial teeth to restore the natural dental function [1]. Conventional dental implants are typically made in metal and metal alloys, where titanium and its alloys have an important role. Besides the high cost of these materials, the traditional manufacturing systems are expensive having in mind the number of implants to be produced and their complex shape [2].

Currently, there is a need to improve the method manufacture of dental implants, making them cheaper and fast manufacturing [3]. In order to investigate alternative cost effective manufacturing methods for producing dental implants, micro metal injection moulding (µMIM) technology was evaluated. µMIM is regarded as very promising net shaping technique for micro parts, due to its advantages for complex geometry, precision and production in great series of implants with high performance, without finishing process [3,4]. The µMIM process have five processing steps, namely: raw material characterization, mixing of powder and binder for feedstock preparation, injection moulding of feedstock into the desired shape, debinding to remove the binder and sintering to give the required properties [5,6]. The µMIM technology can help to produce cheap dental implants. However it can be necessary to improve the rate of osseointegration e.g. through implants coated with nanohydroxyapatite (nanoHA) with or without silicon addition. There are studies reporting that HA doped with specific elements (titanium) has advantage in

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biological process [7]. Therefore, HA based coatings were selected due to their good performance in osseointegration behaviour. In the present work, were produced dental implants by μMIM process from austenitic stainless steel powders (SS 316L). The selection is related to a lower cost of powders SS 316L than Ti alloys (in proportion of 1:3) [2,4]. The sintered dental implants were physical and mechanical characterised and the torque strength of implants was evaluated using as counter body a bovine rib. The dental implants produced were coated by nanoHA with various contents of silicon. After coating, the implants were characterized in what concerns the hardness and Young's modulus. The bioactivity of the coated and uncoated samples was assessed by immersion tests, for different periods of time in simulated body fluid (SBF).

1. Experimental Methods

1.1. Materials

In this work, the metal powder used was water atomized 316L austenitic stainless steel - SS316L (from Epson Atmix Corporation®) and the multi-polymeric binder used composed by a mixture of polyolefin waxes (from Atect®). The HA target (99.9% purity from Cerac, Inc) was used for the deposition of thin films as received or patch worked with silicon wafers (10x10 mm^2, purity 99.5%, from Cerac, Inc).

1.2. μMIM

The thermal characterization of the binder is very important to know the melting and degradation temperatures, to define the processing conditions for mixing and injection, as well as the binder removal cycle.
The feedstock was optimized as it is described by F. M. Barreiros et al. [8]. The mixture of metallic powder and binder was optimized by torque rheometry technique in Brabender Plastograph mixer, for suitable evaluation of the critical powder volume concentration (CPVC), at programmed temperature and rotational speed. After optimization, it was possible to select the suitable powder:binder ratio for produce the feedstock and this was evaluated by controlling the torque value during the mixture process and by SEM micrographs. Finally, the feedstock was granulated into small granules for promote the homogeneity and to facilitate the feed when carried out the injection moulding, into a mould cavity with shape of dental implants in Arburg 270C injection moulding machine.
The debinding and sintering thermal cycles, were carried out in a high temperature oven of Termolab model Superkenthal, under controlled atmosphere of 95% argon and 5% hydrogen (argon can protect the samples from reacting with oxygen and the hydrogen can reduce the oxide and produce a clean metal surface). The debinding cycle was based on binder thermal analysis and the sintering conditions were carried out according to the selected powder.

1.3. Deposition

The dental implants produced by μMIM technique were coated with thin films of hydroxyapatite (HA) and hydroxyapatite doped with different silicon contents (HASi). These coatings were sputtered on a surface of dental implant using a rf magnetron sputtering equipment (Edwards Coating System E306A) and argon as the sputter gas (deposition parameters: $d=32x10^{-2}$ W/mm^2; P=1.2 Pa; t=5400 s). For the doped thin films the HA target was patch worked with 2 and 4 silicon wafers.

1.4. Techniques of characterization

The powder and the binder characteristics were evaluated concerning as: density using helium picnometry on AccuPyc 1330 – Micromeritics; particle size distribution using Mastersizer 2000 – Malvern; phases compositions by X-ray Diffraction (XRD, equipped with Co Kα radiation) on X'pert – Philips; morphology in a Scanning Electron Microscopy (SEM) on ISM 5310 - JEOL and the thermal behaviour: Differential Scanning Calorimetry (DSC)/Thermogravimetric Analysis (TGA) on Setaram Setsys
The green samples were analyzed by SEM and Infinite Focus Measurement (IFM) on Alicona. After sintering, the surface implants were analyzed by SEM and IFM, and the microstructure was evaluated after polishing and chemically etching (HCl + HNO_3 + Glycerol) according ASTM E407/07. The mechanical properties of the dental implants were evaluated, e.g. hardness and Young's modulus were evaluated in the center and periphery by nanoindentation technique (Nanotest, Micro Materials) carried out with a diamond Berkovich indenter with 10 mN load. The values of nanoindentation and Young's modulus were obtained through the application of Weibull statistics to the experimentally measured data.

The mechanical characterization of dental implants was achieved after an insertion torque test using a surgical hand-piece with a multiplying rate of 32:1 mounted on a SEM Nouvag® surgical unit with torque control that was performed by an implantologist (through torque strength test and used diverse surgical equipments: surgical motor – NOUVAG SEM, micro-motor and contra-angle – NOUVAG 32:1).

The structure of the coatings was analyzed by XRD and the morphology by SEM. The mechanical properties of the coatings, e.g. hardness and Young's modulus were evaluated through the same machine, with 0.30 mN load. The load was low due to the thickness of the coating witch varied from 400 to 2400 nm. Thus, the measurements were taken from a depth that avoided the influence of the substrate's mechanical properties on the measured data.

The bioactivity of the coated and uncoated surfaces was assessed by soaking them in PBS at 37 ºC, 100 rpm for 28 days. The samples and duplicates were removed at days 7, 14, 21 and 28, rinsed with distilled water and dried at room temperature prior to SEM observation.

2. Results and discussions

2.1. µMIM

The SS 316L powder has a density of 7961 kg/m^3 and having a particle size distribution of d_{10} = 2.99 µm, d_{50} = 7.68 µm and d_{90} = 12.63 µm (bimodal distribution). The fig. 1 shows the water atomized powder, mostly spherical that means a shape factor close to 1. The XRD analysis shows that the SS 316L is a biphasic system constituted by austenite (A) and ferrite (F) phases (fig. 2).

The binder is composed of polyolefin waxes and the density was 970 kg/m^3. The thermal analysis occurred under argon atmosphere, from room temperature to 800 ºC at a heating rate of 10 ºC/min.

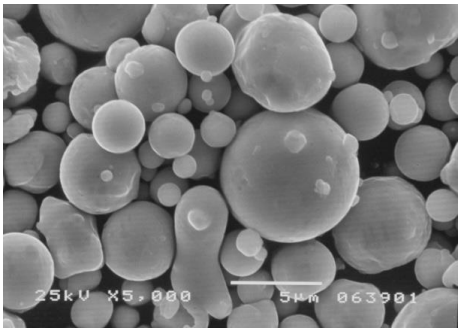

Fig. 1. SEM micrograph (5000x) of SS 316L.

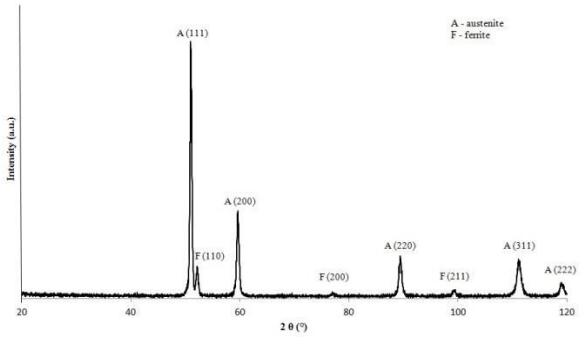

Fig. 2. X-ray diffractogram of SS 316 L.

The fig. 3 shows that loss of weight (TGA curve) begins at 200 ºC and ends with total removal of binder at 475 ºC. On the other hand, the DSC curve shows some initial peaks that correspond to melting and evaporating of some components of the binder, while others peaks correspond to their degradation, manifested by weight loss. The range between 350 ºC and 450 ºC is an endothermic peak that requires special attention in the debinding step, because there is a significant loss weight, about 40%.

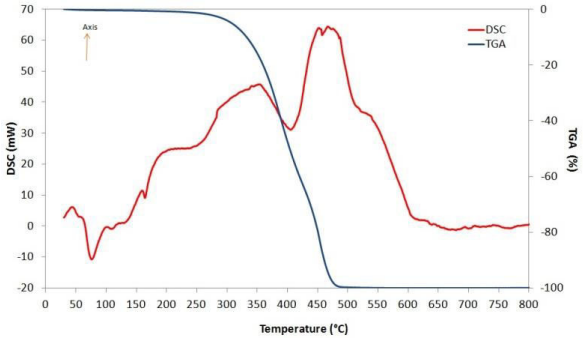

Fig. 3. TG and DSC curves of binder.

Based on binder thermal analysis, the temperature selected for optimization of the mixture was 180 ºC and with a rotation speed of 30 rpm. The torque value increasing with the powder additions and the fig. 4 shows four distinct regimes of shear stress variation with the powders content, corresponding to 50-52, 52-57, 57-62 and 62-64 percent in volume. During the first and second regimes, the torque value increases slightly with the powder content. Then, in the two last regimes, this increase was more significantly. The best powder:binder ratio for producing the feedstock was 60:40 (% vol.) because have high solids content and the torque value (i. e. relative density) seems appropriate for injection moulding step.

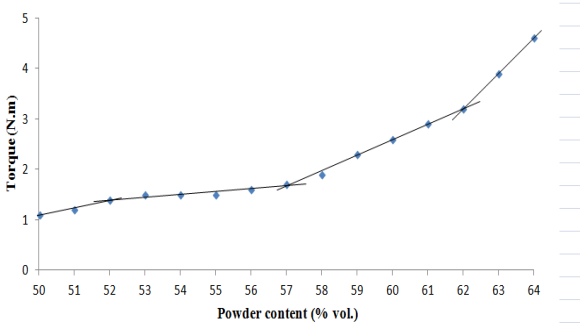

Fig. 4. Torque value versus powder content.

After optimization, the mixtures were produced during 30 minutes until the torque value achieved the stability (indicating of homogeneity) and the torque of the mixture 60:40 % in volume was approximately 2 N.m (fig. 5).

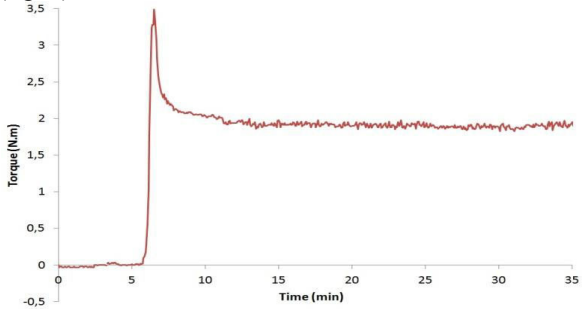

Fig. 5. Torque versus time of mixture 60:40 (% vol.).

The fig. 6 shows the feedstock, where it is possible to highlight that the powders are surrounded by the binder.

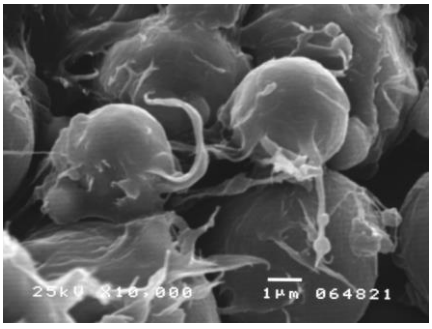

Fig. 6. SEM micrograph of feedstock (10000x).

The injection parameters selected to produce the "green" samples were a mould temperature of 60 ºC, an injection temperature of 150 ºC and an injection pressure of 10 MPa. The fig. 7 a) shows the green dental implant in real scale and the surface quality was evaluated using IFM (fig. 7 b)).

Fig. 7. "Green" implant a) in real scale and b) analyzed by IFM.

In fig. 8 shows also the surface quality of the implant thread of the green by SEM.

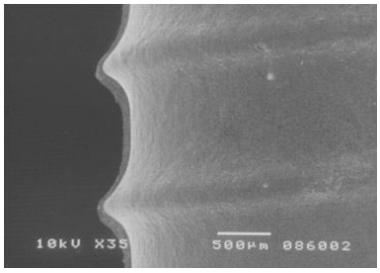

Fig. 8. Implant thread "green" (SEM 35x).

The debinding cycle occurred up to maximum temperature of 700 ºC, the heating rate of 1 ºC/min and under controlled atmosphere of Ar+H_2. Before and after the debinding cycle, the samples were weighed to assess the rate removal and the removal of binder was higher than 92 %. The SEM micrograph of "brown" samples shows that are not visible residues of the binder after debinding (fig. 9).

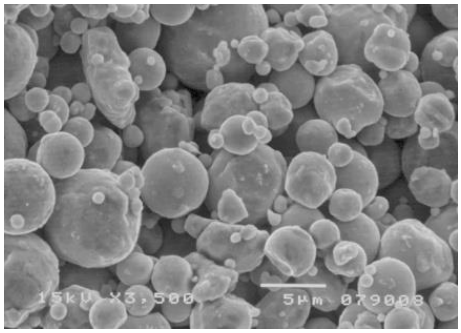

Fig. 9. SEM micrograph of "brown" component (3500x).

The sintering cycle was performed under the same atmosphere used in the debinding, with a heating rate of 10 ºC/min, up to maximum of 1250 ºC. After sintering, the common aspect of the implant is shown in fig. 10 a) and the morphology details by IFM in fig. 10 b).

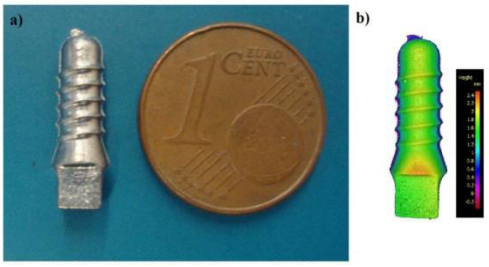

Fig. 10. a) Net shape implant and b) Implant view by IFM.

During debinding and sintering steps, the dental implants suffered shrinkage of 13 % up to 14 % (fig. 11). It is also noteworthy, that the surface quality of the final dental implants had a bright aspect, similar to a polishing surface. The density of the sintered components measured by helium pycnometry has a medium value of 7590 kg/m^3 (95.3 % of theoretical density), which is close to density of initial material.

Fig. 11. "Green" and final dental implants.

From the microstructural analysis of the sintered components (fig. 12) it is possible to check that the metallography is the predictable for the austenitic stainless steel. The grain size is homogeneous and there are vestiges of porosity indicated by the arrows.

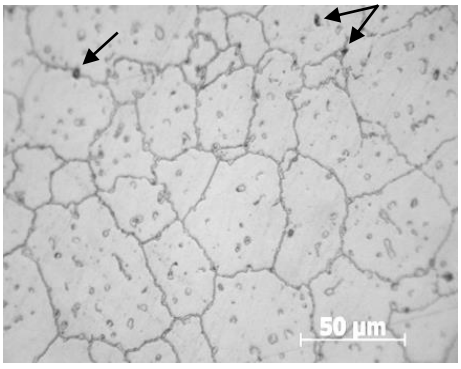

Fig. 12. Microstructures of the sintered implant (400x).

The hardness (H) and Young's modulus (E) of the dental implants were assessed in center and periphery (fig. 13), and the values are resumed in table 1. The hardness has a coherent value in distinct areas of implant and the Young's modulus values are in according to the values of the same steel after casting.

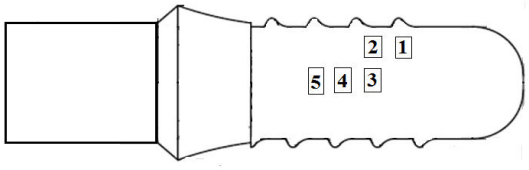

Fig. 13. Outline of indentations areas.

Table 1. Hardness (H) and Young's modulus (E) values of dental implant

	H (GPa)	E (GPa)
1	4.50 ± 0.28	200.22 ± 17.28
2	4.69 ± 0.20	200.11 ± 11.52
3	4.68 ± 0.52	196.34 ± 20.81
4	4.84 ± 0.39	201.99 ± 12.39
5	4.72 ± 0.23	202.99 ± 7.89

2.2. Binary tests

To evaluate the mechanical behaviour of dental implants manufactured from SS 316L powders by µMIM an insertion torque test was carried out. This was performed by an implantologist, which sequentially used drills of different diameters (2.2; 2.8 and 3.5 mm) with rotation speed of 850 rpm to prepare the implant bed (fig. 14). In order to create a spiral to introduce the implant, it was used another drill with 4.1 mm diameter (similar to diameter of dental implant) and a speed of 30 rpm (fig. 14). The fig. 15 shows the final dental implants tested.

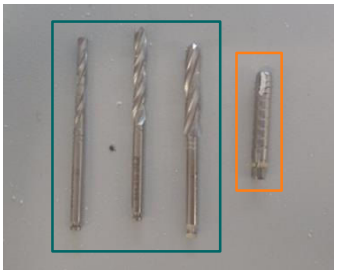

Fig. 14. Drills used.

Fig. 15. Final dental implants tested.

A bovine rib was selected for this test due to its cortical and spongy regions, to be similar to a human mandible bone - equivalent to bone type 2 (fig. 16 a)). The sintered dental implant was introduced in rib with speed of 30 rpm and the maximum torque was less than 0.27 N.m (fig. 16 b)). After removal the implants from the rib, they were physically unchanged, which means that the material adequately supported the insertion forces and for that may be adequate for this application (fig. 16 c)). The test showed that dental implants produced from SS 316L powders by μMIM may be mechanically suitable for this application. This represent a new way to producing great series dental implants that means faster and cheaper than the conventional manufacturing processes.

Fig. 16. a) Bovine rib, b) with implants and c) without implants.

2.3. Coatings characterization

Once mechanically suitable to be implanted in bone, dental implants must present a surface with osseointegration features. Therefore the dental implants were coated with three types of thin films, with or without silicon additions (HA, HASi(2) and HASi(4)). The X-ray diffractograms (fig. 17) revealed some diffraction planes that could be identified as HA, according to ICDD card 09-0432. This characterization highlight the nanocrystalline structure of the monolithic HA thin film and that the introduction of Si induces amorphization of the coatings.

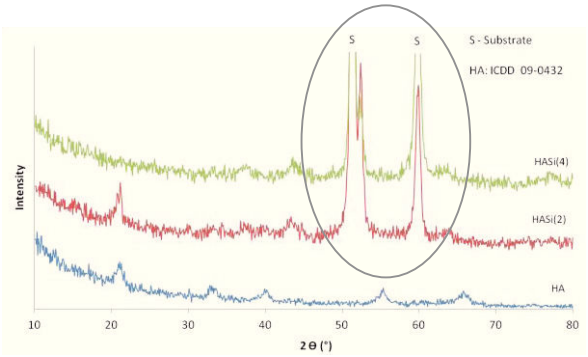

Fig. 17. X-ray diffractogram of different coatings.

The surface morphology (fig. 18) of all samples indicates homogeneous and smooth surfaces regardless of the chemical composition.

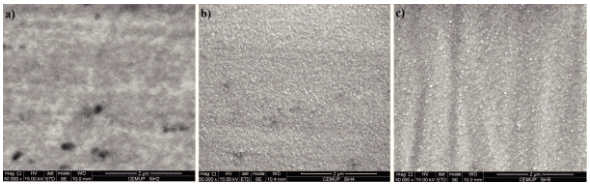

Fig. 18. SEM micrographs of a) HA, b) HASi(2) and c) HASi(4).

The hardness (H) and Young's modulus (E) of the coatings were measured (table 2). The HA doped with Si firstly show a decrease of hardness and Young modulus, but for HASi(4), the values are similar to the sputtered HA.

Table 2. Hardness (H) and Young's modulus (E) values of coatings

	H (GPa)	E (GPa)
HA	4.2 ± 0.3	126.8 ± 7.9
HASi(2)	1.8 ± 0.2	95.3 ± 12.7
HASi(4)	4.9 ± 0.3	127.5 ± 19.8

In order to assess the bioactivity of the modified surfaces the samples were evaluated by SEM after in vitro tests in SBF (fig. 19). All the samples present apatite like (Ca-P-O) precipitate layer onto their surfaces in opposition to the 316L unmodified surface. These preliminary results indicate that the modified surfaces are able to induce an improved biological performance when compared with the bulk 316L.

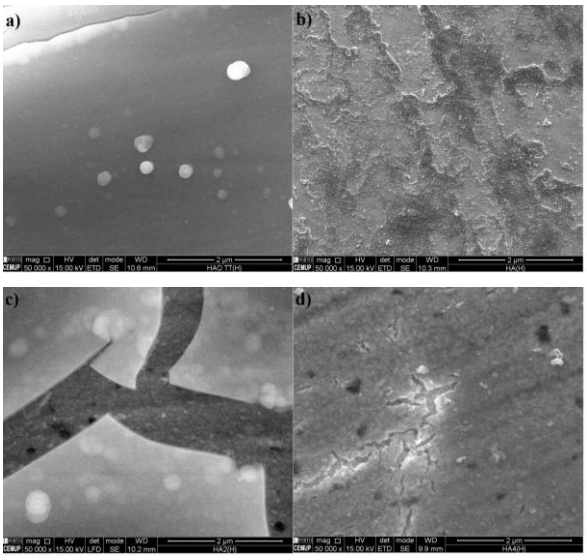

Fig. 19. SEM micrographs of a) 316L, b) HA, c) HASi(2) and d) HASi(4) after 28 days in SBF.

Conclusions

The μMIM is suitable to produce dental implants. The surface of sintered dental implant has a bright aspect and a good workmanship which means that processing conditions were correctly selected. The 316L austenitic stainless steel and the process selected are appropriate for dental implants and this was demonstrated by torque strength test. However, an implant in SS 316L has not a good osseointegration, to overcome this problem, the presence of a coating that must promote this mechanism is a good option. Thin films of hydroxyapatite doped with silicon improve the bioactivity. A new strategy is opened up for manufacturing much less expensive of dental implants, called "implants for crisis", provided that the implant's surface assures a similar or superior osseointegration to the conventional implants commercially available.

Acknowledgements

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