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THE STUDY OF PROTOTYPES OF DENTAL IMPLANTS OBTAINED BY THE TITANIUM POWDER INJECTION MOLDING PROCESS: *in vivo* STUDY

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Abstract. The production of titanium parts from powder metallurgy is one of the tendencies of modern metallurgy, since it allows obtaining structures with complex geometries and controlled porosity. The purpose of this study was to produce two types of dental implant prototype, and compare them biologically. Smooth surface prototypes were obtained, by the conventional turning process and porous surface prototypes using Metal Injection Molding (MIM). The prototypes were implanted in rats that were euthanized after 3 weeks, and the bone/implant interface was analyzed. The results showed that all prototypes were clinically stable at the end of the healing period, but those produced by the MIM process presented a significantly higher percentage of osseointegration (bone/implant contact) than the milled prototypes in the same healing period. It is concluded that the bone tissue grew independent of type of implant, enabling quick, rigid fixation already in the third week of the healing process.

Introduction

The technological importance of titanium as a biomaterial has been exhaustively researched in the last 50 years, in order to improve the integration between implants and bone tissue [1]. Mechanical-metallurgical properties, such as low modulus of elasticity, biocompatibility, high resistance to corrosion, good chemical and thermodynamic stability of the titanium oxide layer, low density, high mechanical resistance and excellent formability favor the union between the implant and bone tissue. [2].

However, the use of titanium and its alloys for dental implants is still limited, since the manufacturing processes use high cost techniques, such as casting and milling [3,4]. This occurs mainly due to the different stages and difficulties in processing, such as the high fusion temperature, reactivity with oxygen at high temperatures, finishing stages and later need for surface treatments in order to acquire a topography that is porous or with microroughness.

Beginning in the 1980s, the success of osseointegration has been based on the modification of the external surface of the implant. The modifications involved range from purely mechanical treatments that aim at increasing the surface roughness all the way to chemical treatments that lead to structural changes in the OXIDE layer [5,6].

The powder metallurgy (PM) technique , for instance, the metal powder molding process by injection, Metal Injection Molding (MIM), is a competitive alternative compared to the conventional manufacturing processes. The properties inherent to the MIM process, such as better surface finish, production of near-net-shape parts, microstructural homogeneity and control of part porosity are extremely relevant for the advance of research in the field of osseointegration, besides contributing to the reduction of the final cost of manufacturing

The MIM process is the result of combining the thermoplastic molding process with the powder metallurgy process. It is advantageous because of the few stages needed for its processing. It is one of the tools to produce small section parts and complex shapes that is undergoing the greatest expansion on the market [7] without the need for later milling or any other finishing process, and it acquires physical characteristics that are difficult to obtain by any other metallurgical process.

This process requires an injectable load (*feedstock*), which is produced by mixing metal powder with an agglutinating system (*binder*) usually composed by waxes and polymers. This

feedstock is injected into a metal die which models the load to the intended shape, generating the so-called "green" part. Later the binder is extracted and thus the so-called "brown" part is obtained. To end the manufacturing process, the thermal treatment of sintering is performed. This is where densification occurs and consequently the part acquires mechanical resistance [8].

Due to these considerations, the purpose of the present paper was to produce, implement and compare, histologically, implant prototypes based on commercially pure titanium (Ti cp), manufactured using the MIM process and the conventional milling process.

Materials and Methods

Prototype production

Twenty prototypes were made using titanium hydride powder by the MIM process. They acquired a naturally porous surface, sintered prototypes. In order to perform a comparative histomorphometric analysis, solid titanium bars were used to make 20 prototypes with a "smooth" surface, milled in a CNC lathe.

The choice of prototype geometry was based on screws similar to those used in Champy® miniplates. This type of geometry presents a larger surface of contact with the bone tissue and provides good primary stability after surgery, thus favoring healing [9]. The schematic geometry of the prototypes is shown in Figure 1.

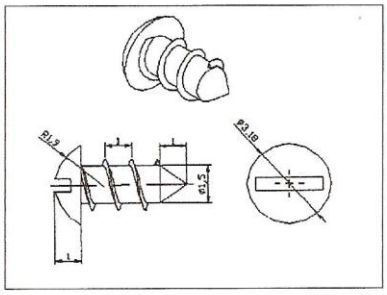

Fig. 1 – Dimensions and schematic geometry of the implant prototype.

Making the die

Based on the determined geometry of the prototype, a die was made to inject the material to be molded. In two rectangular bars, size 2.5 x 10x 80mm, three cavities were made shaped like a screw cut along the axis and an injection canal, as seen in figure 2.

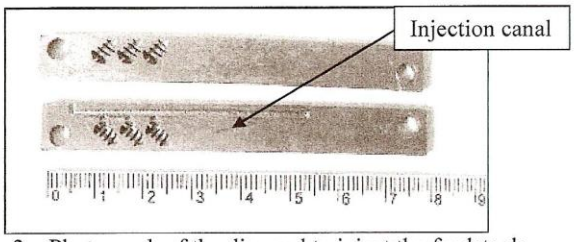

Fig. 2 – Photograph of the die used to inject the feedstock

Obtaining the injection load (feedstock)

The mixture of powder with the binder system was performed in an oil-heated Werner and Pfleiderer mixer at 190°C, for approximately two hours, the time needed to homogenize the mixture. After cooling, this load was taken to the Seibt knife mill to pelletize the feedstock so that it was ready to be injected.

The composition of the feedstock used can be seen in table 1.

Table 1 – Feedstock composition.

Component	Proportion [% in mass]
Titanium hydride	85.00
Polypropylene	5.25
Stearic Acid	0.45
Paraffin	9.30
Total	100.00

Injection process

The die with its two bars fitted one over another, was introduced into a mold holder (Figure 3) of the ARBURG ALLROUNDER 220S® high pressure injector. This equipment allows working at a maximum injection pressure of 250 Mpa, maximum temperature of 350°C and maximum injection volume of 30 cm^3 (Fig. 4).

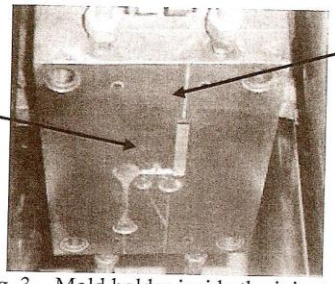

Fig. 3 – Mold holder inside the injector.

The arrows show the cavity where the die was placed for feedstock injection and above, the injection canal.

Fig. 4 – ARBURG® ALLROUNDER 220S model high pressure injector at LdTM.

The feedstock produced in the Mechanical Transformation Laboratory was injected according to the parameters shown in table 2.

Table 2– Injection parameters.

Parameters	Magnitude
Pressure	150Mpa
Upset pressure	120Mpa
Counter Pressure	0Mpa
Dosage flow	15cm^3/s
Flux	35cm^3/s
Cooling Time	15s
Injection temperature	170°C
Mold temperature	150°C

Debinding

The debinding was performed in two stages:

- chemical extraction of waxes by solvent,
- thermal extraction of polymers in an inert controlled atmosphere of Argon 5.0 to avoid oxygen or nitrogen contamination..

Chemical extraction

The binders in the chemical extraction phase were removed by immersion of the green parts in hexane solvent at 60°C in a thermostatic bath. This temperature was chosen, since above it the hexane would boil (69°C) and this would cause distortions in the parts. At this stage the parts lost 10% of their mass compared to the injected part (green part).

Thermal extraction

The binder thermal extraction curve (figure 11) takes into account the thermal degradation temperatures of the polymers based on the "thermogravimetric analysis (TGA)" curve. The parts are sintered in the same thermal extraction cycle.

Sintering

Figure 5 shows the thermal extraction curve and sintering, respectively, where the 432°C level refers to polypropylene extraction (PP) and the 500°C one indicates the titanium dehydring procedure. The temperatures above 500°C are related to sintering (700°C pre-sintering and 1300°C sintering). The heating rate imposed on the cycle is 2°C/min, and each of the levels lasted one hour. The total process time was approximately 15 hours, ignoring the cooling time (around 6 hours).

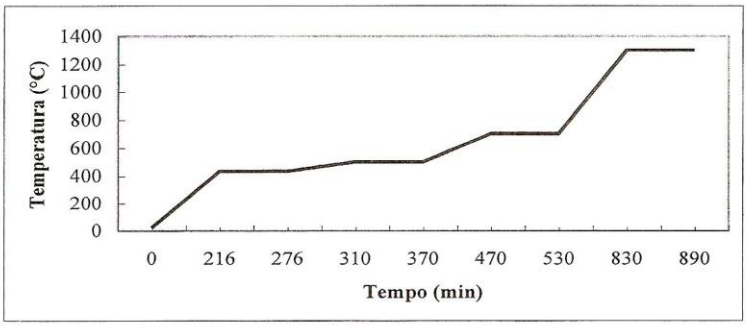

Fig. 5 – Thermal extraction curve and sintering.

Microhardness test

In order to evaluate the quality of the mechanical properties obtained in the sintered samples, microhardness tests were performed and their results were expressed on the Vickers scale. The measures were performed in a Strüers Microdurometer with a 500 gf load [10].

Calculation of porosity

The porosity of the sintered part is a characteristic inherent to the MIM process, but that can substantially change its mechanical properties [11]. The porosity was determined according to Equation 1. The density considered for titanium was 4.51g/cm^3, according to Donachie [12].

An Explorer HAUS precision balance was used to obtain mass and the principle of Archimedes to calculate the volume.

$$\text{Porosity} = (1-d_p/d_m) \times 100\% \qquad (1)$$

Where:
d_p is the density of the porous part
d_m is the density of the solid part.

Discussion and Results

Although titanium is accepted as biomaterial, new treatment techniques are being researched to modify the surface of the implants, as alternatives to speed up the osseointegration process, especially in its initial phase. [13,14,15,16].

The methodology of post-metal injection developed in this work was based on the studies by Brème [17] and Gálio [18] to constitute a competitive alternative compared to the conventional manufacturing processes. With this technique it is possible to control porosity by using different grain sizes and variations in sintering temperature.

The evaluation of the osseointegration indexes showed that the sintered prototypes obtained a significantly better result in the prototypes with a milled surface. This result may be due to the fact that the porous surface has a contact area greater than the milled surface and that it stimulates cell proliferation.

The satisfactory clinical and histomorphometric results of this research may also be explained by the observations performed by Bobyn [19], since they report that for bone growth to occur inside the pore, this must have a maximum diameter of approximately between 50 and 400 μm, where the minimum value is very close to the findings in this study. With this dimension blood vessels can develop in the structure of the pore, allowing bone growth.

Although the MIM can use recycled raw material, such as milling scraps, or titanium slivers to minimize costs, a quality control process must be performed to comply with current legislation.

Prototypes obtained using the MIM process

The main characteristic of the MIM process is obtaining naturally porous parts, and there is no need to treat or coat the surface after milling, as in the techniques reported by Teixeira [6] and Maeztu [20].

During the MIM process, three types of parts were obtained: green part (after injection) a fragile part in which the polymer contained in the binder offers the mechanical resistance of the part; brown part (after the binder is extracted), extremely fragile, handling it must be avoided; and final part (sintered part). The final size of the sintered part can be seen in Figure 6, where, on the right side is the milled prototype.

Figure 6 shows this variation among the three stages of the process with a milled part. The relationship of the variation of mass and time to perform chemical extraction (debinding) may be seen in figure 7. Considering that the feedstock is made up of approximately 10% wax and lubricant, the loss of mass in chemical extraction is within the expected range.

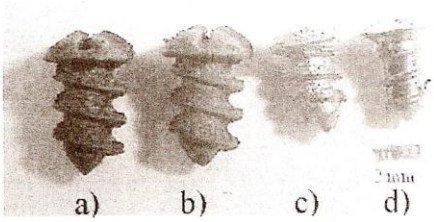

Fig. 6 – Sequence of screws from left to right: green part (a), brown part (b), sintered part(c) and milled part (d).

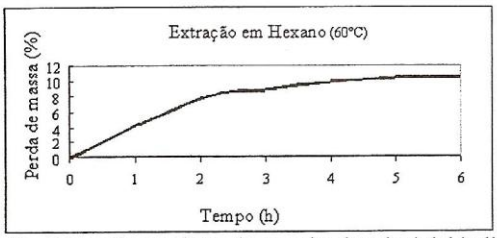

Fig. 7 – Loss of mass from the part in chemical debinding.
(Extraction in hexane Loss of mass ,Time (h)

Microhardness test

Three sintered prototypes were used for this test in which the results were expressed by a profile of mean hardness, shown in Figure 8. This profile was obtained from a radial cut in the screw and the reference "0" of the data collection points was the center of the screw cross-section in its median region.

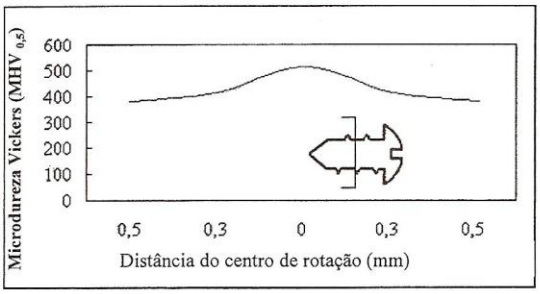

Fig. 8 – Distribution of the microhardnesses performed in the screws, from the center of the screw as shown in the schematic included in the graph.
Vickers microhardness. Distance from the center of rotation

Table 3 shows the data collected in the three samples tested, considering that the microhardness of the sample varies as regards the rotation axis.

Table 3 – Values (in Vickers $_{0.5}$) of the microhardness test of the samples per sampling point.

Point [mm]	Sample 1	Sample 2	Sample 3	Mean	Standard Deviation
0.5	370.9	341.6	381.5	364.6	16.9
0.3	410.9	418	409.2	412.7	3.8
0	518.2	508.5	508.5	511.7	4.6
0.3	416.2	419.7	432.5	422.8	7.0
0.5	345.6	366.5	369.4	360.5	10.6

Part Porosity

Porosity tests were performed on five sintered prototypes. Based on the variables measured (mass and volume), the prototype density was obtained, and, consequently, the porosity value of the material manufactured. These data are shown in Table 4.

Table 4 – Mean Porosity obtained from the prototypes of sintered implants.

Sample	Mass [g]	Volume [cm^3]	Density [g/cm3]	Porosity [%]
1	0.0449	0.0105	4.2762	4.97
2	0.0410	0.0095	4.3158	4.09
3	0.0388	0.0091	4.2637	5.25
4	0.0407	0.0097	4.1959	6.76
5	0.0445	0.0100	4.4500	1.11
Mean	**0.0420**	**0.0098**	**4.3003**	**4.44**

According to Bathomarco [21], the level of porosity must be controlled because the cells need anchorage points on the implant surface to begin proliferating and ensure osseointegration. Thus, it is accepted that there is an ideal porosity to fix the implant and the MIM technique allows achieving this goal.

Histomorphometry

The results obtained by observing the histological sections showed that both the porous prototypes and the milled ones were fixed to the animal bone tissue, since all surfaces evaluated showed variable bone growth in contact with the surface of the implant prototypes. Figure 9 and 10. The prototypes of the MIM process obtained an average of 83.37% bone-implant contact, while the milled ones had 55.83% in the 3-week period.

Fig. 9- Sintered prototype 3 weeks after implant

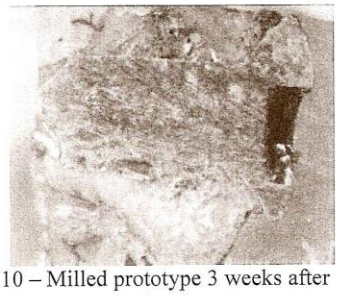

Fig. 10 – Milled prototype 3 weeks after implant

Conclusion

- The MIM process proved technically feasible as an alternative for the production of sintered parts for dental implants, highlighting the reduction in the number of manufacturing stages, and cost reduction for purchasing raw materials compared to conventional processes.
- Bone growth occurred independent of the type of surface, but a significantly higher percentage of bone-implant contact occurred in the sintered prototypes.
  - The mean pore size found agrees with reports in the literature.

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