Study of the suitability of a commercial hydroxyapatite powder to obtain sintered compacts for medical applications

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Abstract. Hydroxyapatite (HA) is a material widely used by the medical community due to its Ca/P ratio is comparable to the Ca/P ratio of bones and teeth, which promotes osteoinduction and osteoconduction processes when in contact with bone tissue, either as volume piece or coating. This work focuses on studying the quality of the commercial HA powder MKnano-#MKN-HXAP-S12 µm, after processing, to obtain sintered compact discs with suitable physical and chemical characteristics for implants applications. The HA powder was processed through calcination, grinding, pressing and sintering to evaluate the effect of such as procedures in the compacts dics quality. The raw powder was characterized by laser diffraction, SEM, XRF, XRD, TGA and DSC while the characteristics of the obtained compact discs were determined by dilatometry and XRD to identify the sintering temperature range, constituent phases, the amorphous content and the crystallinity degree, parameters that allow determining their suitability for implants applications. Although, it was not possible to obtain sintered compacts with the suitable chemical composition and without fractures, this work allowed to identify the parameters that determine the suitability of a HA powder to obtain sintered compacts for medical applications, as well as the characterization protocol that allows the evaluation of such parameters.

1. Introduction

The Hydroxyapatite (HA) is a bioactive material because its Ca/P ratio is close to the Ca/P ratio of bones and teeth, this has turned the HA in a suitable material for clinical applications either as dense material or as coating over implants. The manufacturing processes of compact ceramics determine its properties and then influence the effectiveness of the processes that make use of these compacts [1]. The most used techniques to form compacts from HA powder are pressing and sintering [2], some others are: hot and cold pressing, hot isostatic and cold isostatic pressing; thermal plasma spraying; conventional, vacuum, spark and loose sintering; induction, arc and electron-beam melting, vacuum melting and casting; and co-precipitation technique.

The publications that study the in vitro behavior of HA sintered compacts report very different results about the microstructural, chemical and mechanical properties of these materials. It has been demonstrated that porous compacts favour the osteoconduction, but are less resistant to applied mechanical charges compared to dense compacts. On the other hand, the osteoinduction improves when the compact is amorphous but the durability of the compact is better as its crystallinity grade increases. Nevertheless, in most cases, the authors describe neither the manufacturing process of the

dense compacts nor its final characteristics [3], [4]. At the same time, it turns out to be unusual that the processing parameters effects in the dense compacts characteristics are evaluated. This work focuses on studying the quality of the commercial HA powder MKnano-#MKN-HXAP-S12 µm, after processing, to obtain sintered compact discs with suitable physical and chemical characteristics for implants applications.

2. Materials and methods

The raw material used for the manufacture of the 2 in diameter HA discs consisted in the commercial HA powder #MKN-HXAP-S12 µm of the international mark MKnano, which reports for this powder 99 % of purity and an average particle size (APS) of 12 µm. The values of the powder processing conditions were taken from the reported values in the consulted literature for the realization of the state of the art: temperature and stabilization time during calcination 1000 ºC for 3 hours, compression force during pressing 500 kN, and temperature and stabilization time during sintering: 1100 ºC for 4 hours [5–7].

To evaluate the raw material and the effect of the identified processing condition, in the compact discs quality, the following characterization tests were realized: laser diffraction of the as-received and calcined powder in a Mastersizer 2000 and Cilas 930E, respectively; dilatometry in a Netzsch DIL 402 PC; Thermo-Gravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC) in a TA Instruments' Universal V4.5A; Scanning Electron Microscopy (SEM) of the MKnano powder particles in a JEOL JSM 6490 LV; X-Ray Fluorescence (XRF) spectrometry of the as-received and calcined powder in a ARL OPTIM' X WDXRF Spectrometer and PANalytical' AXIOS, respectively; and X-Ray Diffraction (XRD) in a PANalytical' XPert Powder and PANalytical' XPert Empyrean Serie II, for the phase identification and quantification by Rietveld and internal standard methods [8]. Fluorite, CaF_2 (32 % wt.), was used as internal standard, complying with the condition of compatibility with the analysis sample proposed by L. S. Zevin in 1979 [9].

3. Results and discussion

3.1. Particle size distribution

The APS increased and the Particle Size Distribution (PSD) decreased in amplitude after the calcination and grinding processes (see Figure 1), this is advantageous in relation to the homogeneity and densification that could be reached during the sintering process from powders [3]. In addition, a major APS implies smaller specific surface area, which can improve the powder manageability during compression.

3.2. Particles morfology

The particles morphology gives an idea about the powder synthesis process. Angular morphologies indicate that the material was melted and grinded and spheroidal morphologies indicate that it was

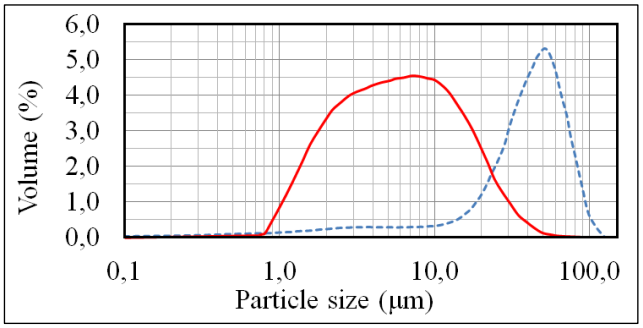

Figure 1. Grinded and calcined powder' PSD, APS 40 µm (dashed line) and as-received powder' PSD, APS 6. 2 µm (solid line).

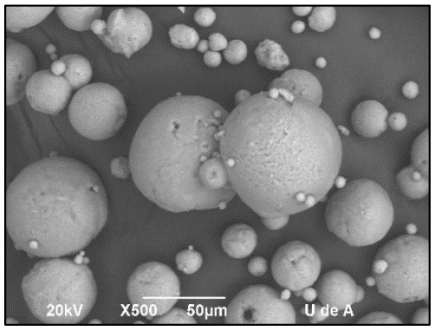

Figure 2. SEM micrography (500X) of the MKnano powder particles sample.

agglomerated and sintered. The fact that the MKnano powder morphology (see Figure 2) is spheroidal turns out to be advantageous, since it is reported in the literature, that this morphology type is ideal for the controlled production of ceramic bodies [10].

3.3. Chemical composition

The powder composition analyzed by XRF (see table 1) indicates that the 99 % of purity reported by the provider is affected by a high content of potassium (K_2O) that stays after the calcination process, which goes to the detriment of the powder quality to be used in medical applications, considering the requests of obligatory fulfillment given by the standard ISO13779-6 [11] about impurities. The potassium content also prevents the determination of the Ca/P ratio.

3.4. Composition in phases and content of amorphous

From the XRD results presented in Figure 3, it was possible: i) to verify that MKnano powder consists of HA, as the provider informed, but also that the apatite is slightly crystalline and is accompanied by an amorphous material, quantified in 17.8 ± 5 % p/p by the internal standard method, and ii) to identify that both thermal treatments, calcination and sintering, drive to the transformation of certain quantity of this amorphous material in a phase constituted by potassium and phosphorus (KH_2PO_4).

Table 1. MKnano powder composition in oxides.

Oxides	As-received powder (% wt.)	Calcined powder (% wt.)
CaO	38.530	46.020
P_2O_5	24.380	34.750
K_2O	13.270	14.286
MgO	0.211	0.330
LOI	23.470	2.160

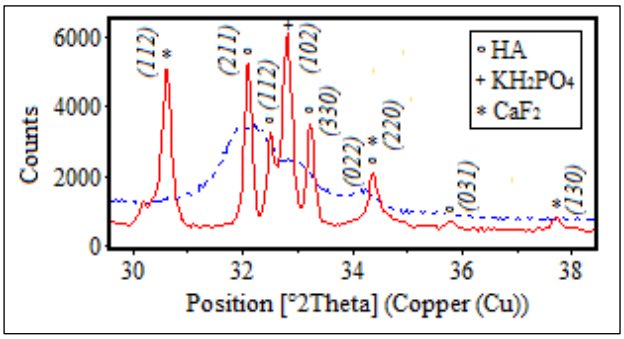

Figure 3. X-ray diffractogram of the grinded and calcined powder (solid line) and as-received powder (dashed line).

3.5. Thermal behaviour

The Figure 4 represents the curve of the powder thermal expansion parameter, which includes the material intrinsic thermal expansion, the contraction for sintering and phase transformations [12]. This information makes possible to identify that the sintering temperatures range for the MKnano powder is between 750 and 1170 ºC because in this range takes place the greater contraction achieved by the evaluated compact, which is an indicator of the least volume that the sample achieves when applying

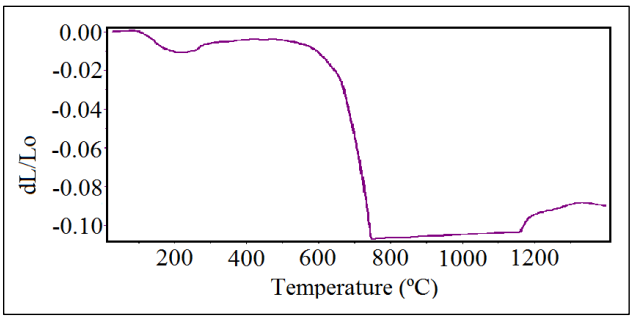

Figure 4. Curve of the HA compact sample thermal expansion.

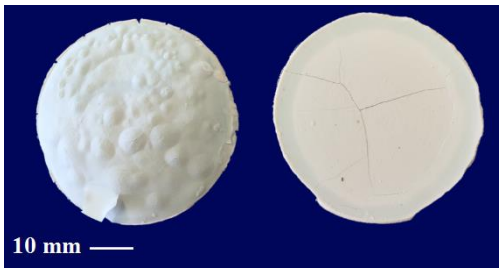

Figure 5. Sintered discs from calcined (right) and as-received powder (left).

thermal treatment. From the Figure 5 is possible to identify that: i) it is indispensable to calcine the powder before sintering, since phase transformations deform the HA compacts and ii) during cooling, there also happen physical phenomena that could fracture the discs.

4. Conclusions

ISO13779-6 standard [11] establishes two statements: i) the HA degradation phases in a powder for medical applications must not be bigger than 5 % wt., and ii) the maximum acceptable limit of traces is 30 mg/kg. This study evaluated the incorporation of a calcination treatment, prior to press and sintering, as a mechanism to remove the agglomeration agent based on potassium and in consequence to make the powder suitable for medical applications. Nevertheless, it was identified that both calcination and sintering thermal treatments conducted to partially transform the raw material in a crystalline phase constituted by potassium and phosphorus degrading in part the crystalline HA and affecting the Ca/P ratio ($1.66 \leq x \leq 1.71$) specified by the standard for powders usable in medical applications. In spite of the undesired chemical transformation of the MKnano powder and the fractures produced as consequence of the undesired chemical composition, this work allowed to identify the parameters that determine the suitability of a HA powder to obtain sintered compacts for medical applications, as well as the characterization protocol that allows the evaluation of such parameters. This procedure can be replicated in future works with commercial or homemade HA powders with the suitable and verified chemical characteristics to manufacture suitable sintered compacts of HA.

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