Research Article

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Spark plasma extrusion of binder free hydroxyapatite powder

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Abstract: This work explores the possibility of manufacturing dense and nanocrystalline hydroxyapatite (HA) large monoliths by spark plasma extrusion (SPE). This method combines uniaxial mechanical compression, high temperature, and electromagnetic field to promote the extrusion and sintering of HA powder in one single step. The results show that the binder-free extrusion of precompacted HA powder is feasible at a temperature similar to the temperature at which nanocrystalline HA shows superplastic behavior. The extrusion continues throughout the sliding and rotation of the particles, and also due to the grain boundary sliding, up to the point where no more material is available, thus producing monoliths of nearly 30 mm in length and 10 mm in diameter. The dehydration and smooth surface of the powder appear as paramount factors to facilitate the HA extrusion without additives. The extruded HA preserved the stoichiometry and nanometric grain size and exhibited preferential microstructural alignment in the direction of extrusion. The material experiences local thermal and pressure gradients during extrusion, producing different densification and hardness along its length. The SPE of HA will benefit the healthcare field by offering new processing approaches of bone substitutes and osteosynthesis devices.

Keywords: hydroxyapatite, spark plasma extrusion, sintering, nanocrystalline, superplasticity, grain boundary sliding, spark plasma sintering

1 Introduction

Hydroxyapatite (HA) is a calcium phosphate ceramic widely known for its clinical applications as bone substitute in orthopedic medicine [1]. A great number of commercially available products based on HA, either pure or combined with other compounds, are clinically used today [2]. Most of these products are porous monoliths since pores promote osteoconductivity [3]. Moreover, HA exhibits a wide range of in vivo degradation rates, ranging from being almost stable (like large grain and pore-free monoliths [4]), to total resorbable, when used as granules or in the porous form [5]. Even when purely synthetic HA powder can be processed in the laboratory either using soft chemistry routes [3,6], or high-temperature synthesis [7], the obtained powder cannot be directly used as an implant, rather the powder requires to be shaped and consolidated into a specific geometry. It is well known that in contrast to metals, ceramics cannot undergo plastic deformation near room temperature due to the chemical nature of their high directional atomic bonding. Therefore, ceramics are unable to accommodate deformations via slip dislocations, piling up stresses, particularly near the microstructural defects such as pores, leading to brittle failure, thus, excluding the production of ceramic objects through plastic deformation. Nonetheless, both

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dislocation movement and partial stress relaxation in porefree ceramics with nanometric grain size are possible at high temperatures, as reported for HA [8]. The plastic deformation of polycrystalline ceramic materials has been reported at elevated temperatures and this property is called superplasticity. Since the discovery of superplastic yttriastabilized tetragonal zirconia [9], superplasticity has been observed to occur in other ceramics, including HA, undergoing 150–486% elongation when heated between 1,000 and 1,050°C at a strain rate between 1.0×10^{-4} and 1.4×10^{-4} s⁻¹ [10–13], concluding that grain boundary sliding (GBS) is the dominant mode of deformation [10]. The following excellent book is recommended to get more details on superplasticity in ceramics [14].

Currently, the extrusion of ceramic powders or powder injection molding is a widespread and successful method for shaping near-net shape products [15]. However, the extrusion of ceramic powders at room temperature requires a binder to convert the powder into a moldable material. Otherwise, the powder requires very high pressure to overcome the frictional forces between particles and flow. Moreover, the green body requires both the elimination of the binder after shaping and high-temperature sintering to convert the powder into a polycrystalline monolith. Although the extrusion of ceramic powders is not a particular case of ceramic superplasticity, it is expected that the combination of high temperature and axial pressure enables the powder extrusion without additives, by promoting particle sliding and probably through simultaneous GBS of the sintered particles. The possibility to shape and sintering ceramic materials in a single step without the need to remove additives is desirable to reduce processing time and cost. In particular, the extrusion of HA will benefit the healthcare field by offering new processing approaches of bone substitutes and osteosynthesis devices in the form of screws.

One way to trigger ion mobility in ceramics, like HA, is through the usage of high electromagnetic field assistance procedures, such as the pulsed electric current sintering (PECS) [16] or spark plasma sintering (SPS) [17]. These methods promote densification of difficult to sinter and/or metastable materials [18]. Although the number of investigations on SPS of HA-based ceramics substantially increased [8,16,17,19–23], the majority of those publications deal with the preparation of coin-like specimens, with a thickness of less than 5 mm and diameters from 5 to 20 mm, which limits their practical applications. A recent adaptation of the SPS process, so-called spark plasma extrusion (SPE), is convenient to produce enlarged materials (bars >60 mm long), such as aluminum, copper, and aluminum–carbon nanotube composites [24–27]. SPE

is therefore a straightforward method for the extrusion of HA at high temperature without the use of additives. This study aimed to produce and sinter, for the first time in one single step long monoliths of HA using SPE, around the temperature that HA shows superplastic behavior.

2 Materials and methods

2.1 Synthesis of HA

Stoichiometric HA (Ca₁₀(PO₄)₆(OH)₂) powder was prepared by the chemical precipitation method. Commercially pure-grade calcium hydroxide and phosphoric acid (JT-Baker, USA) were separately dissolved in pure and deionized water at a concentration of 1 M. The phosphoric acid solution was slowly added (10 mL/min) into the calcium hydroxide solution and thoroughly mixed using magnetic stirring (300 rpm) until a stable pH of 8 was reached. Steady agitation was practiced for 12 h at room temperature for maturation. The precipitate was subsequently washed using distilled water and centrifuged at 6,000 rpm for 20 min. Later, it was resuspended in 2L of distilled water and was kept in constant agitation, while being heated up to 110°C till water evaporated. The obtained nanoparticle HA powder was pulverized and calcined in air at a heating rate of 5°C/min till 700°C, keeping it for 2 h and then allowed to cool down inside the stove. Powder The powder was then kept in a desiccator to avoid hydration. Differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) were conducted on a DTA-SDT apparatus of TA-Instruments, USA, model Q-600, at a heating rate of 10°C/min to determine the chemical and physical changes in the powder during calcination up to 1,200°C.

2.2 SPE

To conduct the HA powder extrusion, a graphite die-set consisting of two end-punches and an extrusion cylinder, as shown in Figure 1, was used. The length of the die-set was limited to the working distance available between the processing electrodes of the commercial Dr. Sinter SPS-device 1050 Sumitomo Co., Japan, used for this investigation. Just before the extrusion, 8 g of HA powder were pre-compacted at 9.5 MPa at room temperature. The obtained green body had the form of a cylinder (20 mm in diameter) with a truncated conical tip (10 mm in the smallest diameter and 5 mm of length) with a total



Figure 1: Scheme of the graphite die-set used to conduct the SPE of HA powder.

length of 30 mm and fitted perfectly in the extrusion die as shown in Figure 1. The green body was sandwiched between graphite paper sheets for easy removal of the product. As already stated, no additives were used for the extrusion.

Once the whole die-set was assembled and covered with graphite cloth to minimize heat losses, it was placed inside the SPS chamber and degassed until an air pressure of 8 Pa was achieved. Figure 2 shows the thermomechanical treatment conducted to extrude the HA powder. The treatment parameters were selected according to previous experience on SPE of copper [27] and considering the



Figure 2: Heating program and loading profile used to conduct the SPE of HA powder.

compressive strength of the graphite used to fabricate the extrusion die (30 MPa). First, an axial preload of 6.5 MPa was applied to the die-set to close the electrical circuit. Then, a heating rate of 100°C/min was continued up to 1,150°C, and then the die-set was allowed to cool down until 800°C. The temperature was kept constant until completing 25 min of treatment. The axial load was increased at a rate of 0.063 MPa/°C from 6.5 MPa to the extrusion load (28.5 MPa) starting when the temperature reached 800°C, *i.e.*, after 8 min of heating. The load was kept constant to complete the thermomechanical treatment. In the last step, the current was cut off and the load was released to allow the extrudate to cool down for 2 h under a vacuum condition before being removed from the die. The temperature was monitored using a K-type thermocouple (maximum operating temperature of 1,200°C) inserted into the half-thickness of the wall at the middle-length of the die (Figure 1). The pulsed electrical current was set to 12/2 ms on/off cycles to match the conventional operational settings of SPS.

2.3 Material characterization

The densities of the extruded monoliths were measured according to Archimedes' principle in distilled water at 25° C. To evaluate the density values at different positions, extrudates were cut into four transversal sections. A theoretical density of 3.16 g/cm^3 for HA [6] was used as reference.

X-ray diffraction (XRD) measurements were carried out to analyze powder and extrudates, with a Bruker, USA, apparatus model ECO – AXS Diffract Plus/D8 Advance, using CuK α radiation and wavelength λ = 1.5406 Å, scan step of 0.017° and 0.3 s as counting step. In the case of the extrudates, the transversally cut samples were polished using diamond suspension till 1µm finish, so that the X-ray analyses were focused in four different positions along the extrusion direction. The crystalline domain size was calculated using the Debye Scherrer equation [28]. The average crystalline domain size was taken from the calculations carried out on the following diffraction peaks: 31.8, 32.9, 39.8, 46.73 and 49.5 degrees in two-theta, typical of HA.

The microstructure of both the extrudates and the HA powder was analyzed by using the scanning electron microscope (SEM, JEOL JCM-6600, Japan), in samples coated with a thin carbon layer to prevent overcharging during observation. In addition, the nanometric size of the HA powder was confirmed by transmission electron microscopy (TEM, JEM-1200EX, JEOL, Japan). Vickers microhardness testing was carried out with a QS Metrology hardness-tester, India, model HMV-G21D, using 980 mN for 10 s. The measurements were performed every 0.5 mm along the extrusion section.

3 Results and discussion

3.1 Characterization of HA powder

The thermal analysis (Figure 3) indicated that the absorbed water was released from 100 to 400° C with a mass loss



Figure 3: TG and DSC curves of the synthesized HA powder.

of around 1.6%. The broad exothermic peak developed from 100 to 700°C suggested partial HA recrystallization, whereas, in agreement with the literature [29], HA decomposition started around 800°C. A total mass loss of 4.4% at 1,200°C was recorded. In agreement with these results, the peak of temperature practiced to aid the extrusion was followed by a moderate reduction of temperature to prevent HA decomposition.

Figure 4 shows the XRD patterns of the HA powder before and after being calcined at 700°C for 2 h. In agreement with TGA and DTA observations, sharper and more defined Bragg peaks were formed after calcination due to partial recrystallization, where the crystalline domain size rose from 56 to 65 nm. Furthermore, after calcination, a change in the powder morphology was observed (Figure 5). The as-prepared HA powder consisted of rough surface aggregates formed by nano-sized particles (Figure 5a), clearly observed in TEM (Figure 5c). After calcination, the nano-sized particles within the aggregates were pre-sintered, leading to smoother particles with nano-grains (Figure 5b). This change in particle roughness upon calcination involves a significant reduction of frictional forces between particles, enabling in the past the binder-assisted extrusion of HA at room temperature [30].

3.2 SPE of HA

An important observation derived from this study is the fact that under the same extrusion conditions, the noncalcined HA powder did not flow, whereas the calcined



Figure 4: XRD patterns of the synthesized HA powder before and after calcination at 700° C for 2 h.



Figure 5: Representative images of the HA powder, SEM images (a) before and (b) after calcination at 700°C for 2 h, and (c) TEM image of the uncalcined powder.

powder produced in average 25 mm length extrudates (Figure 6). Note that the length of the extrudate was similar to the length of the pre-compacted powder evidencing the flow and densification in parallel of the powder. Moreover, the length of the extrudates was limited in this study by the size of the SPS chamber, although the results suggest that it is possible to produce larger monoliths. Possible factors that influence the powder flow are as follows: (1) a smoother surface of the calcined powder favoring particle slipping and rotation [31], (2) a hydrated layer on HA crystals [32] that can generate steric attractions or even promote early sintering, consequently increasing the load needed for extrusion, and (3) part of the energy may be used for physicochemical modifications of the non-calcined powder leaving less energy for extrusion [33].

Figure 7 shows a typical SPE curve. A negative displacement was observed between 25 and 650°C due to the thermal expansion of the material. The onset of extrusion was at 650°C, *i.e.*, before the rise of the axial pressure and at a temperature significantly below the temperature that HA has been reported to be superplastic (1,000–1,050°C) [10–13]. The extrusion proceeded at an almost constant rate with the increment of temperature and pressure up to 950°C (16 MPa). Then, the extrusion rate decreased, and the extrusion continued at a constant pressure even during the cooling segment from 1,150 to 800°C. The extrusion reached the maximum displacement approximately after 15 min.

The physical aspect of obtained extrudates is shown in Figure 6, together with a schematic representation of the relative density (RD) attained at different zones



Figure 6: Physical aspect of the HA extrudates obtained by SPE: (a) representative image of an extruded sample showing a fracture at the head generated upon its release from die, (b) the same specimen after polishing demonstrating the variety of colors developed due to the different densification levels attained. The samples were white-bright at the tip (highly porous) and translucent at the head (high dense). (c) Sketch with the RD attained at different zones of the monolith. The scale bars in (a) and (b) correspond to 10 mm.



Figure 7: Displacement *vs* time SPE curve of calcined HA. Relevant temperatures and axial pressures are indicated. Please refer to the text for an explanation.

of the monolith. The average RD measured for the whole monolith was 85%. The cross-section of the extrudate displayed different colors and brightness, which were the function of the degree of densification [34]. A translucent zone was observed at the head of the specimen. This zone was exposed to a higher temperature along the process due to the thinner cross-section of the upper endpunch favoring heating, and consequently, both recrystallization and sintering took place in this zone, reaching an RD of 99%. In agreement with Morsi et al. [24], this zone corresponds to the SPS zone, in which the powder only experienced compaction and sintering without extrusion. In contrast, since no opposition force existed at the extrusion aperture, a significant lower densification (RD of 64%) was observed at the tip of the monoliths, apart from the fact that this area was the colder zone during SPE. The extrusion zone (which concentrates the major

deformation of the material) is between the head and the tip of the extrudate. The extrusion zone exhibited two parts, a dark zone closer to the SPS head with an average RD of 96%, and a white zone close to the tip with a RD of 77%. Unlike SPE of metals [24], the extrusion zone developed lower densification than the head of the specimen, probably because of gradients of temperature due to the lower thermal conductivity of the ceramic and limited powder densification induced by plastic deformation [35,36].

Figure 8 shows the microstructure of the extrusion zone with an RD of 96%. The images were acquired by analyzing the interior of a pore revealed after polishing the monolith; therefore, the lines indicate the flow of the material, aligning the microstructural features nearly parallel to the extrusion direction. Microstructural texturizing induced by the extrusion was confirmed by XRD (Figure 9).

3.3 Crystalline features of the extrudates

In general, the XRD patterns obtained from the different zones of the extrudate were indexed solely as HA with no signals of other phosphates, such as tricalcium phosphate or pyrophosphate (Figure 9). This is in agreement with the reported thermal stability data for stoichiometric HA, which in the range of temperature of the present study mostly presents dehydration to form oxyapatite $(Ca_{10}(PO_4)_6O)$ [29]. However, clear differences in crystal orientation were observed between the zones with different densifications. Particularly, in the extruded part of the monolith, where the deformation is accumulated, the planes (120) and (300) at the 77% of RD zone and the planes (002) and (004) at the 96% of RD zone exhibited a significant increase in their intensity, respectively. This



Figure 8: Representative SEM images of the extruded HA monolith at different magnifications (a), (b) and (c). The images were acquired inside a pore in the extrusion zone with an RD of 96%. Arrows indicate the direction of HA flow during extrusion.



Figure 9: XRD patterns of different zones along the extruded HA monolith. The XRD pattern of the calcined HA powder is included as reference. Preferential crystal orientation is observed in the extruded zone.

suggests a preferential orientation of the crystalline lattice in the *a*- and *b*-axis in the former, and along the *c*-axis in the latter case [34]. In contrast, both the head and the tip of the extrudate presented a typical XRD pattern of HA without any clear evidence of preferential crystalline orientation. Therefore, instead of associating the crystal orientation with differences in the local sintering temperature, the orientation was related to the alignment of the material when passing through the reduction of the extrusion die. This matches the fact that both the head and the tip of the extrudates did not undergo enough deformation to induce some crystalline orientation. High perpendicular alignment of the *c*-axis of the HA crystalline lattice concerning the direction of the uniaxial mechanical compaction pressure was observed in transparent HA specimens sintered without extrusion by PECS [16]; nonetheless, the sintering temperature and pressure were higher than in the current conditions.

There was a moderated grain growth in the extruded HA monolith as evidenced by the size of the crystalline domains. The larger crystalline domains (size of 270 nm) were observed at the head of the extrudate (the SPS zone [24]) as a result of higher local temperature, whereas the smaller domains (size of 108 nm) were observed at the tip. Therefore, the extruded HA retained a refined microstructure similar to conventional SPS processing [8], with the advantage that SPE enables the production of significantly larger monoliths. Although the present results are a proof of concept of the feasibility of HA mechanical processing by SPE, the results have not been thoroughly

optimized and further improvement and control of the process are needed. This includes numerical simulation of the process to correlate the electric and stress fields with the temperature distribution and densification of the material during the extrusion flow. Furthermore, to fabricate, for example, intramedullary locking nails or screws, HA should have to a develop certain degree of plastic deformation to increase the mechanical strength. Strain hardening was observed during the tension test of HA and was argued to be caused by grain growth [8]. Preventing residual porosity that can compromise the strength of load-bearing implants is also an open task. Nevertheless, the development of open porosity, or even materials with gradient porosity, can be highly valuable to fabricate implants with tuned osteoconductivity and degradation rate. Further work concerning the effects of HA crystal orientation on bioactivity and resorption is yet to be conducted.

3.4 Hardness profile of the extrudates

The Vickers microhardness profile (Figure 10) was performed as a first approach to study the mechanical properties of the HA extrudates. This test was selected due to the heterogeneity in the density of the monoliths, the nanometric grain size, and also due to the restrictions on the sample size. Currently, the preparation of larger and homogeneous extrudates that allow the determination of



Figure 10: Vickers microhardness profile along the longitudinal section of the HA extrudate.

bulk mechanical properties and fabrication of useful medical implants are sought. The hardness values range from 6.7 GPa at the head with 99% of RD to 0.5 GPa at the tip which only developed sintering adhesions at the contact points between the particles. The hardness of the densest zone is within the range reported for HA sintered by SPS [19] and conventionally sintered up to an RD of 92.5% [37]. The hardness profile demonstrates the differences in densification of the material, preventing the discernment of an effect of the crystal orientation. Furthermore, the four zones previously described developed different local densification, since the hardness did not present a plateau in any of them. Therefore, the densities in Figure 6 correspond to the average density of the respective zone.

Figure 11a shows a typical hardness indentation in the 99% RD zone disclosing radial cracks running out from the four corners of the footprint impression and delamination. The cracks present slight deflected profile, few branches, and have a length greater than 25 μ m as a signal of quasi-brittle fracture mode. Meanwhile, Figure 11b shows an indentation in the 77% RD zone. In this case, the footprint impression has edge cracks with no visible radial cracking, presumably due to the presence of the higher amount of large pores that arrest the crack propagation.

3.5 HA extrusion mechanism

From the results obtained in this work and considering the information reported for the SPE of metallic materials [24], a possible extrusion mechanism for the HA powder is presented herein. The ceramic powder did not undergo plastic deformation at low temperature, consequently, the particles are just aggregated with minor reorganization producing a poorly packaged green body. During SPE the compacted powder experiences shear stresses



Figure 11: Representative images of residual hardness impressions on the cross-section of the HA extrudate (a) at the head zone (RD of 99%) and (b) at the extruded zone with RD of 77%.

as a result of the mechanical pressure. With the assistance of high temperature and the electric field, the powder yields throughout the sliding and rotation of the particles and possibly due to GBS as observed in other nanocrystalline oxides [36]. The temperature, the high specific surface area of the powder, and the compaction force activate the powder densification in parallel to the extrusion [35]. The flow of the powder aligns the particles in a preferential direction, which led to an oriented crystal growth during sintering [16], as evidenced by the change of the relative intensities of the diffraction peaks concerning to the XRD pattern of the SPS zone. The plastic deformation of the material by GBS [8] and the material densification assisted by deformation enable extrusion to continue up to the point where no more material is available.

4 Conclusion

HA SPE was carried out for the first time. The dehydration and smooth surface of the HA powder were identified as paramount factors to enable the extrusion without the addition of any lubricant or binder. The extrusion started at a temperature considerably below the temperature that HA shows superplastic behavior. The length of the extrusion is currently limited by the size of the extrusion chamber. The extruded HA preserved the stoichiometry and nanometric grain size, exhibiting microstructural alignment in the direction of extrusion. The hardness profile developed in the extrudate is a consequence of the degree of densification achieved locally, rather than the influence of the grain size or the strain induced in the HA. SPE is foreseen as a new alternative processing approach useful for the fabrication of elongated HA implants.

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