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Bioceramics: spark plasma sintering (SPS) of calcium phosphates

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Abstract. Calcium phosphates (Ca-P) are major constituents of calcified tissues, and are also extensively used for the elaboration of biomaterials. However, the usual high-temperature sintering processes generally lead to strong alterations of their chemical, physical and biological properties. Spark plasma sintering (SPS) is a non-conventional sintering technique based on the use of pulsed current, enabling fast heating and cooling rates, and lower sintering temperatures are often observed. The sintering of several orthophosphates (DCPD, amorphous TCP, beta-TCP, OCP, HA and biomimetic nanocrystalline apatites) by SPS was investigated in order to track potential advantages of this technique over usual Ca-P sintering methods. Special attention was given to the SPS consolidation of highly bioactive nanocrystalline apatites.

Introduction

Calcium phosphate ceramics exhibit an excellent biocompatibility and show osteoconductive properties. They are widely used as bone substitute materials and replace autologous grafts or allografts. These ceramics are generally obtained by sintering at high temperature for several hours, and they exhibit a very limited surface reactivity. These harsh conditions do not enable the use of metastable calcium phosphate phases, yet utilized in other biomaterials applications (bone cements, coatings). This is the case of the hydrated phases dicalcium phosphate dihydrate (DCPD), octacalcium phosphate (OCP) and nanocrystalline apatites.

In particular, nanocrystalline apatites are biomimetic compounds. They are the main constituent of bone mineral and nature has learned to use all the characteristics of their surface and bulk reactivity [1]. They are also considered to be at the origin of the biological activity of orthopedic materials [2]. The surface reactivity of such phases was related to the presence on the nanocrystals of a hydrated layer involving mineral ions in non-apatitic chemical environments [3-5]. However the processing of such apatites while preserving their nanocrystalline nature is delicate. Several methods have been attempted such as low temperature hardening from gels, associations with macromolecules [6] or cements setting [7], however in all cases the mechanical properties proved too weak to allow for a use in bone loading sites. An interesting property of the surface hydrated layer is to favor crystal-crystal interactions. Such interactions have been described as a "crystal fusion" process in vivo. They open interesting properties in material science. The possibility to use the high ion mobility of the hydrated layer to consolidate nanocrystals assembly has been established recently as solid ceramic-like materials could be obtained at very low

temperature by low temperature uni-axial pressing [8]. The materials obtained at 200°C compared well, regarding mechanical properties, with those obtained by traditional sintering at much higher temperatures (1100-1250 °C), but corresponded to a lower densification ratio.

Only very few studies of apatite sintering using spark plasma sintering (SPS) have been performed to-date, and most of them were carried out at high temperature (900-1100 °C). In these cases, SPS sintering was shown to be more efficient when HA powders with small particle size were used, and the compacts exhibited excellent mechanical properties [9]. The formation of transparent apatite ceramics with interesting surface properties has also been reported [10] and generally SPS-sintered HA showed superior surface reactivity in simulated body fluids (SBF) tests, often considered to represent the biological activity [11].

One of the aims of this work was thus to investigate the feasibility of very low temperature consolidation of nanocrystalline apatites by using the SPS technique, which is based on a non-conventional heating source (electrical current through a conducting matrix). This could indeed open a new field related to the making of ceramic-like materials using the surface properties of hydrated apatite nanocrystals, with good mechanical properties and mimicking the bone mineral.

Additionally, the SPS sintering of other major calcium orthophosphates (HA, beta-TCP, amorphous-TCP, DCPD and OCP) was also investigated for a first identification of the potential advantages of this sintering technique as compared to conventional ones.

Materials and Methods

Synthesis of Starting Materials. Dicalcium phosphate dihydrate (DCPD) was synthesized by double decomposition of calcium nitrate tetrahydrate and ammonium di-hydrogenphosphate, in the presence of ammonia. After 5 hours of maturation, the suspension was filtered, washed and freeze dried. Amorphous tricalcium phosphate (TCPam) was prepared by double decomposition of calcium nitrate tetrahydrate and di-ammonium hydrogenphosphate in the presence of ammonia. The precipitate was filtered, washed, freeze dried and stored at low temperature (-18 °C). Beta-TCP was obtained by calcination of TCPam in air, at 900 °C for 24 hours. Triclinic octacalcium phosphate (OCP) was prepared by hydrolysis of DCPD in the presence of di-ammonium hydrogenphosphate, at 37°C. The suspension was filtered, washed, freeze dried and stored at low temperature (-18 °C). Stoichiometric hydroxyapatite (HA) was prepared by adding a solution of ammonium phosphate into boiling solution of calcium nitrate in the presence of ammonia. The precipitate was filtered, washed and dried. Nanocrystalline apatites were synthesized by double decomposition of calcium nitrate and an excess of di-ammonium hydrogenphosphate. After maturation for one day in the mother solution, the precipitate was filtered, washed, freeze dried and stored at low temperature (-18 °C). This sample is referred to in the text as "hap-1d".

Sample Characterization and Mechanical Testing. X-ray diffraction (XRD) was used to determine the crystal structure of the samples, using an INEL diffractometer CPS 120 and the monochromatic CoK_α radiation (wavelength: 1.78892 Å).

Fourier-transformed infrared (FTIR) analysis was used for complementary phase identification and the experiments were carried out on a Perkin Elmer 1600 spectrometer with a resolution of 4 cm^{-1} , using the KBr method.

The chemical composition of selected samples was determined by complexometry for the determination of the calcium content, by spectrophotometry for the total phosphate content.

Due to the size and shape of the SPS graphite matrices, the sintered materials exhibited a disk-shape. Therefore, usual compression tests could not be performed and mechanical testing was carried out using diametral compression test, also referred to as Brazilian disk test [12]. In such experiments, an increasing force (F) is applied on the disks placed vertically until rupture. This

leads to tensile strain perpendicular to F, and the related tensile stress (σ), that is characteristic of the mechanical strength of the disk, is related to F by the equation:

$$\sigma = \frac{2F}{\pi DH} \quad (1)$$

where D and H are respectively the diameter and height of the disk.

Spark Plasma Sintering (SPS). The spark plasma sintering experiments were performed on an SPS 2080 Sumitomo Coal Mining equipment. Pulses of 3 ms of continuous current were applied, with varying intensities. Temperatures below 800 °C were measured by means of a K thermocouple. Above 800 °C, a built-in pyrometer was used. Powder samples were placed in an 8-mm graphite matrix and introduced in the treatment chamber under low mechanical pressure aimed at insuring the matrix stability. The samples were then subjected to secondary vacuum, unless otherwise specified, and heated until spontaneous densification of the powder. A mechanical force of 2.5 kN was then applied uni-axially on the sample and the temperature was kept constant until completion of the sintering process. Fast cooling ($\sim 100^\circ\text{C}/\text{min}$) and release of the mechanical force were then operated.

Results and Discussion

High-temperature stoichiometric Ca-P phases HA and beta-TCP. After introduction of the powdered samples into the SPS treatment chamber, the temperature was raised until observation of a natural contraction of the powder. At this point, the temperature was stabilized and the mechanical pressure of 2.5 kN was applied. This phenomenon occurred at 950 °C for HA and 850 °C for beta-TCP. In these conditions, the sintering stage at the stabilized temperature lasted respectively 5 and 10 minutes. A first remark can be done on the temperatures needed for the sintering of these phases, especially in the case of HA where temperatures over 1000 °C are required under more usual sintering conditions (e.g. hot pressing). Also, the durations of sintering processes are strikingly lowered in comparison with usual methods. These observations are in perfect accordance with first SPS attempts reported in the literature [9-10].

The relative densities obtained for HA and beta-TCP sintered by SPS in the above-cited conditions were found to be close to 81% in both cases, and the tensile stress determined from Brazilian mechanical tests were $\sigma = 16$ MPa for HA and $\sigma = 11$ MPa for beta-TCP. It was not attempted to optimize the densification of such stoichiometric phases in this work, however other authors [9-10] showed that further increase of the temperature of the SPS chamber could raise the relative density of the obtained compacts to more than 99%.

XRD analyses indicated that both phases remained unchanged after SPS treatment. In particular, no preferred orientations were observed as relative intensities were similar to those of the initial powders and to the JCPDS data. Likewise, no obvious modifications of the FTIR spectra were detected.

Hydrated stoichiometric Ca-P phases: DCPD and OCP. DCPD, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, was first located in the SPS sample chamber. Then the temperature was raised, as above, under vacuum. However, an increase of gas pressure was rapidly observed with the rising temperature, betraying the partial decomposition of the initial powder, accompanied by gaseous release (water vapor). XRD analysis performed after heating DCPD by SPS at 150 °C indicated indeed its transformation into the anhydrous phase DCPA, CaHPO_4 , and FTIR spectra also showed the decrease of the intensity of the bands around 3500 and 1630 cm^{-1} relative to water, explaining the gaseous release

observed. Additional SPS experiments were then carried out under nitrogen. However, in all cases, the initial DCPD powder dehydrated into DCPA.

The possibility to prepare compacts based on DCPA could present some interests in the biomaterials field as this phase is already used in the elaboration of some bone cements [13]. However, the disks obtained after SPS treatment of DCPD at temperatures between 150 and 220 °C did not show sufficient mechanical strength for handling (tensile strength, Brazilian test: $\sigma = 0.3$ MPa). SEM analysis of the disks indicated a modification of the initial plate-like DCPD crystals into more rounded morphologies. Despite some agglomeration of such crystals, large voids existed between them, even at 220 °C, explaining the poor overall mechanical strength. Further exploration of optimal SPS conditions was out of the scope of this work focused on hydrated Ca-P phases.

OCP was subjected to the SPS conditions and natural contraction of the powder occurred around 150 °C. Completion of the densification was observed after 5 min at this temperature. The disk obtained was characterized by a relative density of 88% and exhibited a tensile strength of 19 MPa. It is interesting to note that this value is higher than the one obtained with stoichiometric HA at 950 °C, despite an extremely low temperature. In such conditions, the phenomenon observed is probably better described as "consolidation" rather than "sintering". Notwithstanding, it enables to prepare disks with high densification levels. SPS consolidation was attempted at 120 °C. However, in this case it was not possible to reach sufficient mechanical strength for disk handling. XRD analysis of the disks obtained at 150 °C showed strong similarities with the crystallographic features of triclinic OCP. However the existence of preferred orientations probably due to the uniaxial compression was obvious. FTIR spectra were recorded on the initial powder and disks consolidated by SPS at 120 and 150 °C. These spectra show the overall characteristic absorption bands relative to triclinic OCP, however modifications of the $\nu_3(\text{PO}_4)$ mode were clearly visible, especially in the higher frequency side. Also, a decrease of the water content was observed after SPS treatment at both temperatures. The results obtained by XRD and FTIR tend to indicate that consolidation of OCP by SPS led to some alterations of the initial OCP phase, but the main characteristics of this phase were conserved. SEM analyses showed a high agglomeration state of petal-like crystals after consolidation by SPS, which is in agreement with the high densification observed.

Amorphous TCP. The above-cited Ca-P compounds were well-crystallized phases, exhibiting well-known long-range order. In contrast, amorphous tricalcium phosphate does not present, by definition, a crystalline structure although it is now well accepted that its short-range structure derives from the association of elementary blocks, referred to as Posner's clusters $\text{Ca}_9(\text{PO}_4)_6$, with water molecules [14].

The possibility to prepare compacts based on amorphous TCP was studied here using the SPS conditions. Temperature of 150 and 200 °C were tested, with varying heating durations. In both cases, XRD analysis performed on the consolidated disks indicated the crystallization of the initial powder into an apatitic phase. No other crystalline phase was observed. First approximations of the crystallite size were obtained applying Scherrer's formula to diffraction lines (310) and (002), leading to platelets of about 265 Å in length and 110 Å wide for an SPS treatment at 150 °C for 13 min. This structural modification from amorphous TCP to an apatite-like compound was also confirmed by FTIR. The presence of a limited amount of OH⁻ groups is shown by characteristic bands at 630 and 3570 cm^{-1} . The absence of secondary phases suggests that the Ca/P molar ratio remained constant throughout the SPS process. In this context, the phase obtained is probably close to apatitic tricalcium phosphate $\text{Ca}_9(\text{PO}_4)_5(\text{HPO}_4)\text{OH}$, although the low OH⁻ content observed from FTIR betrays the presence of vacancies in the structure.

Observation of the consolidated disks obtained in these conditions showed agglomerates only partially linked together, thus exhibiting a large intergranular porosity, which could explain the

poor mechanical strength observed (Brazilian test, $\sigma = 5$ MPa for 6 minutes at 150 °C). The increase of the duration of the treatment to 13 min led however to a tensile stress of $\sigma = 12$ MPa indicating the possibility to improve the mechanical resistance of consolidated disks arising from SPS treatment of amorphous TCP.

Nanocrystalline apatites. The consolidation by SPS of biomimetic nanocrystalline apatites matured one day (sample hap-1d) in the synthesis solution was investigated. Under SPS conditions, preliminary tests show that the spontaneous densification of the powder started around 150 °C and ranged up to 190 °C. The disks obtained at 180 °C did not show sufficient mechanical resistance. The following experiments were then set to 200 °C with varying durations of treatment. The tensile stress ranged from 18 to 25 MPa for a heating time of 3 minutes from room temperature to 200 °C followed by a plateau at 200 °C for 2 minutes. Interestingly, these σ values are close to those obtained with HA, in spite of extremely short heating times. The corresponding relative density was then close from 70%. When the mechanical force is only applied at the end of the 2-min step at 200 °C, the mechanical strength was found to decrease to about 9 MPa. Likewise, pre-compaction of the powder at room temperature before SPS heating led to an important drop of the tensile stress (ca. 3 MPa). These results point out the correlated effect of temperature and mechanical pressing for the SPS consolidation of immature nanocrystalline apatites. SEM micrographs of the SPS consolidated disks show a high apparent cohesion of the original agglomerates, which is in agreement with the good mechanical properties found.

The XRD pattern of the consolidated disks obtained by SPS treatment for 2 minutes at 200 °C corresponded to a poorly crystalline apatite, although comparison with the pattern of the initial powder indicated an increase of the degree of crystallinity after SPS treatment. No other crystalline phase was discerned. The average crystallite dimensions were estimated applying the Scherrer formula to lines (002) and (310), leading to a length close to 260 Å and a width of about 80 Å as compared to 220 and 55 Å, respectively, for the starting powder. These trends point out an increase of the crystallite sizes due to SPS treatment, however the increase of the crystallite length is noticeably lower than the one observed after more conventional hot pressing treatments, even at low temperature: 295 Å for a treatment at 200 °C for 15 min. Therefore, the SPS process leads to a lower alteration of the initial nanocrystalline powder.

FTIR analysis of SPS consolidated nanocrystalline apatites indicate partial loss of water and the appearance of sharp absorption bands characteristic of apatitic OH⁻ vibrations (Fig. 1).

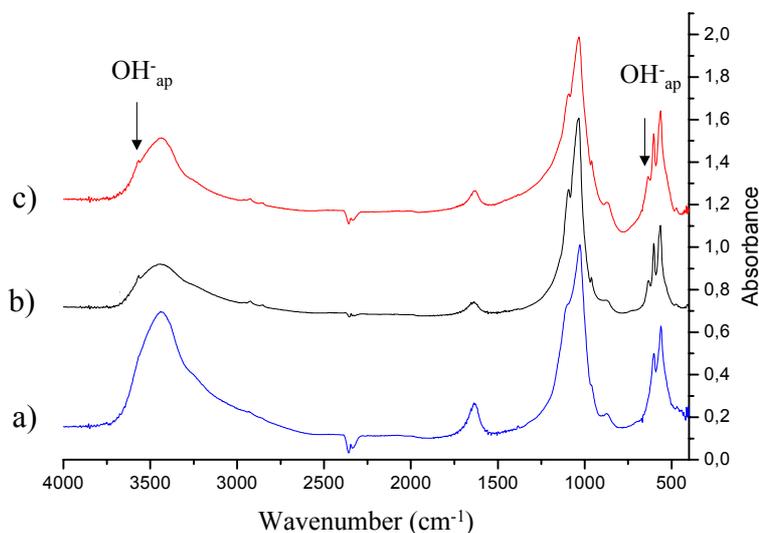


Figure 1: FTIR spectra of hap-1d: a) initial powder, b) after hot pressing (15 min at 200 °C) and c) after SPS consolidation (2 min at 200 °C)

These elements are in accordance with XRD conclusions. The evolution does not involve any variation of the Ca/P ratio of the apatitic phase. The formation of OH⁻ ions can thus be interpreted by an internal hydrolysis of PO₄³⁻ ions as suggested by Heughebaert [15]:



However, this water loss stays lower than the one observed after hot pressing processes, even at low temperature (200 °C for 15 min) as shown in Figure 1. Also, interestingly, at no point was the presence of pyrophosphate phases observed by FTIR after SPS treatment, in contrast with hot-pressed disks where traces of pyrophosphates are often detected. This phase purity represents another advantage of SPS consolidation of nanocrystalline apatites.

Summary

The SPS sintering/consolidation of major calcium phosphate phases used in the biomaterials field was investigated. HA and beta-TCP could be sintered at temperature as low as 950 and 850 °C respectively, and these values are much lower than those reported for conventional sintering techniques. After SPS treatment, hydrated phases were found to lose part of their constitutive water. In the case of OCP, the triclinic structure could still be evidenced although some alterations of the phosphate chemical environments were observed. In contrast, even in neutral atmosphere, it was not possible to consolidate DCPD as total dehydration occurred giving rise to DCPA. SPS consolidation of amorphous TCP led to its complete crystallization into poorly crystalline apatite. SPS treatment of nanocrystalline apatite powders (maturated one day) led to partial loss of water and the increase of the degree of crystallinity and crystallite dimensions. However, these alterations were limited in comparison with conventional sintering such as hot pressing, even at low temperature (200 °C).

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