Journal of the European Ceramic Society 16 (1996) 429–436
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0955-2219/96/$15.00

0955-2219(95)00123-9

Synthesis of Hydroxyapatite-Based Powders by Mechano-Chemical Method and their Sintering

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(Received 18 April 1995; revised version received 28 June 1995; accepted 14 August 1995)

Abstract

Ceramic hydroxyapatite (HA) is on the way to gaining credit as one of the most promising and diversified materials for employment in surgery, thanks to its good characteristics of biocompatibility and bioadaptability. The main and probably unique deficiency of these materials obtained by traditional methods consists in its weak mechanical resistance, that does not allow their use when even low loading is involved. To improve the mechanical properties of HA-based ceramic bodies additions are normally necessary.

In this paper the authors propose a method to prepare powders and composite ceramic bodies with a matrix comprising HA. The powders are produced by the utilization of a simple and economic mechano-chemical method. The composite ceramic bodies are easily obtained by simple firing of the powders at a suitable temperature (1250°C). The powders, after sintering, give products that show a flexural strength of more than 100 MPa in standard samples. This value is significantly higher than that usually attainable with present commercially available powders (60 MPa). The transformation in the components (HA and β-tricalcium phosphate) of the composite ceramic arises from the nature of the powders, consisting of highly defective HA.

The mechano-chemical process is described together with the employed procedures specifically followed for reactive milling of starting powders. The preparation conditions of defective HA powders and properties acquired through such a method are reported. By this method an intimate mixing of β-tricalcium phosphate (β-TCP) inside the HA matrix is obtained that easily allows the preparation of ceramic bodies with reproducible properties, with no necessity for additions and mixing procedures, that could lead to inhomogeneity.

1 Introduction

Hydroxyapatite (HA) is the main inorganic compound of hard tissues such as bones and teeth of vertebrate animals and humans. Consequently HA was readily considered as a bioactive material for artificial bone substitution because of its biocompatibility, and chemical and biological affinity with bone tissue. In the past many different methods were proposed to manufacture HA by chemical synthesis. Particular care was given to wet synthesis starting from separate precursor compounds containing Ca^{2+} and PO_4^{3-}, respectively (see, for example, Refs 1–4).

Many other methods of HA preparation were devised: in the search for an extremely simple one, for β-tricalcium phosphate (β-TCP)[5] and then for HA, a new synthesis method based on dynamic grinding was developed. This method, applied to HA, is the subject of this work and allows us to synthesize a defective HA powder simply by wet-milling a mixed slurry of $CaHPO_4 \cdot 2H_2O$ and $CaCO_3$. The amount of defects depends on the ratio of the reacting powders and on the physical condition of synthesis. A particular choice of these two physico-chemical conditions has led in the past to workers obtaining a calcium-deficient HA[6] by a mechano-chemical method which, for crystallization by firing at ~720°C, led to a total transformation in β-TCP.[7] This initial work on HA synthesis showed that defective powders of HA can be easily obtained by mechano-chemical methods.

The principle on which dynamic synthesis during grinding is founded, relates to the energy provided by the impaction that mill balls exert on powder grains constrained towards the internal wall of the jar, making them react through the setting up of either an interdiffusion mechanism among different grains or intimate chemical reaction of molecules among themselves. The mechano-chemical method is based on the deep squeezing and crushing of powders in the limited surface area of the spherical segment adjacent to the contact point of any milling ball on the container wall (the jar). The physico-chemical conditions needed to shift a chemical reaction towards the required products can be the change of two fundamental parameters: temperature and/or pressure.

In the mechano-chemical process no high variation of temperature is implied, but high values of pressure are reached by that fraction of powder caught between the wall of the jar and the contact area of each milling sphere. The pressure exercized on the bottom part of a cylindrical section of the rotating jar arises mainly by the load coming from gravity forces of all the balls that are arranged in this cylindrical section. Centrifugal force is not practically implied because of the low rotation speed. In order to start the reaction process, it is quite likely that a threshold pressure value should be attained, below which the reaction cannot occur.

In this work we synthesized defective HA by a mechano-chemical method with specific physico-chemical conditions, different from those of a previous paper,[7] to obtain a non-calcium-deficient apatitic compound. The final target was to obtain defective HA-based powders mechano-chemically to give rise to an intimate HA/β-TCP composite ceramic after sintering. To show the importance of the intimate powder mixture on the strengthening of the final ceramic material obtained, the deliberate addition of Al_2O_3 and SiO_2 was also carried out.

2 Materials and Methods

To produce HA, the starting materials were brushite ($CaHPO_4{\cdot}2H_2O$) and anhydrous calcium carbonate ($CaCO_3$) powders. The reagents were selected from the commercial market (Carlo Erba, Milan). The milling device for the mechano-chemical reaction consisted of a Teflon jar and zirconia (ZrO_2) balls. For this study a milling jar made with Teflon was utilized because they are cheaper than zirconia ones utilized in previous papers[5–8] and are easily produced 'in house'.

An 800 g batch of balls was utilized for the usual ball mill (280 r.p.m.), while 340 g were employed for the planetary ball mill. At the usual ball mill, the milling process continued for 48 h, whereas for the planetary ball mill only 4 h are needed. The powders extracted from the mill were placed in a drying oven for a drying period of ~12 h at 90°C. The obtained powders were submitted to microcalorimetric examinations, to X-ray diffraction (XRD) and to infrared spectrometric (IR) analyses, after having fired them at different temperatures.

Table 1 summarizes the main operative parameters, that were chosen from among many experimental ones as those which brought the best results of bending strength of the manufactured ceramic samples prepared in a standardized manner using the obtained powders. All the powders were prepared maintaining a Ca/P molar ratio of 1·67. This table reports only a limited number of different powders, each one specifically coded, obtained under the different conditions described, including the most significant ones. In this paper the authors have used the die pressing method to prepare the samples in the physico-mechanical tests.

To test the quality of the obtained powders, bar-shaped samples were produced by the pressing method with all the synthesized powders: the pressing conditions were 444 $kg_f\ cm^{-2}$ applied on a 45 × 4 × 3 mm die. The bars were fired at temperatures between 1000 and 1400°C for 1 h. Flexural strength tests on the as-fired samples were performed by a four-point bending method (Instron 1195).

3 Results

A Teflon jar was employed to produce HA mechano-chemically synthesized powders for this work. It was observed that the synthesis with this kind of jar requires a time (48 h) twice that necessary when using the zirconia jar. The Teflon jar undergoes a certain degree of surface erosion during rotation. Most of it sublimates with pyrolytic decomposition over 400°C, as thermogravimetric analyses have shown. However no traces of fluorine were detected by micro-chemical analyses

Table 1. Preparation condition of hydroxyapatite powders

Powder code	*Apparatus*	*Container jar material*	*Milling balls material*	*Milling time (h)*	*Introduced water (wt%)*	*Powder content of slurry (%)*	*Distinguishable phases by XRD**
A-2	Ball mill	Teflon	ZrO_2	24	80	20	a-HA,DCPD,$CaCO_3$
HOTP	Ball mill	Teflon	ZrO_2	48	87	13	a-HA
D-1	Ball mill	Porcelain	Al_2O_3	24	80	20	DCPD,$CaCO_3$
C-4	Planetary ball mill	Teflon	ZrO_2	4	80	20	a-HA
C-10	Planetary ball mill	Porcelain	ZrO_2	3	80	20	a-HA,m-ZrO_2 c-ZrO_2,DCPD

*a-HA = Large band peaks of hydroxyapatite; m-ZrO_2 = monoclinic zirconia; c-ZrO_2 = cubic zirconia; DCPD = $CaHPO_4{\cdot}2H_2O$.

on the obtained powders heated over 600°C. Consequently, the calcination process must completely remove it. Teflon debris, if present, can be easily sieved off before any thermal treatment. The powders obtained after synthesis are characterized by low crystallinity, with XRD spectra that exhibit large band peaks (1° wide on a 2θ scale) clearly belonging to apatite alone. We have coded this quasi-amorphous or low crystalline system as *a*-HA. However, it is not possible to exclude the presence of other calcium phosphate–carbonate compounds in the amorphous state, which are not detectable by XRD analysis. This uncertain state goes on till about 600°C. The samples are characterized by a high specific surface area: after optimal calcination (700°C, 1 h) they appear perfectly crystalline but still extremely fine-grained (Table 2).

XRD analysis on powders calcined at different temperatures up to 1350°C allowed us to evaluate the crystallographic degree of purity of the obtained calcium phosphate system. By comparison of the overlapping peaks (0.2.10) and (217) having d = 2·880 Å belonging to β-TCP with the d(211) = 2·814 Å one belonging to HA, it was possible to calculate intensity ratios. By comparison with samples prepared by intimate mixing of β-TCP and HA in known proportions, it was possible to define the percentage ratios reported in the curve of Fig. 1. The trend for this curve is not constant and the ratio β-TCP/HA changes with temperature. The minimum level of β-TCP arising from the heated mechano-chemical defective HA powders prepared for this work is exhibited, approximately, in the range 700–1160°C, as shown in Fig. 1. The minimum fraction of β-TCP is produced at 1150°C. The maximum amount of TCP was evaluated to be ~30% on powders heated at 1350°C.

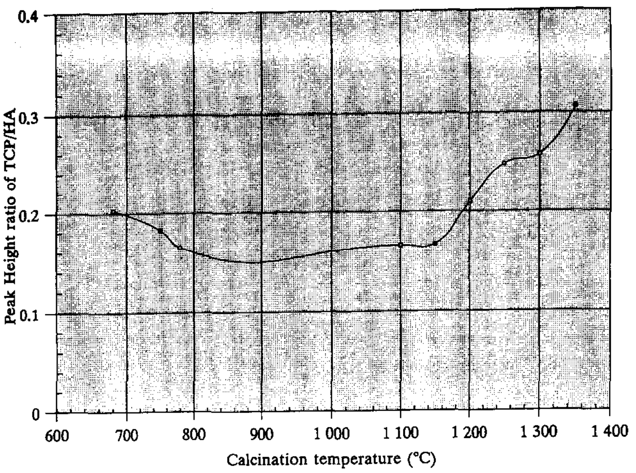

Fig 1. Relationship between XRD intensity ratios of TCP/HA and calcination temperature.

On the same powders calcined at various temperatures, FTIR spectroscopic analysis was also performed: the IR spectra obtained at the most significant temperatures are reported in Fig. 2. As

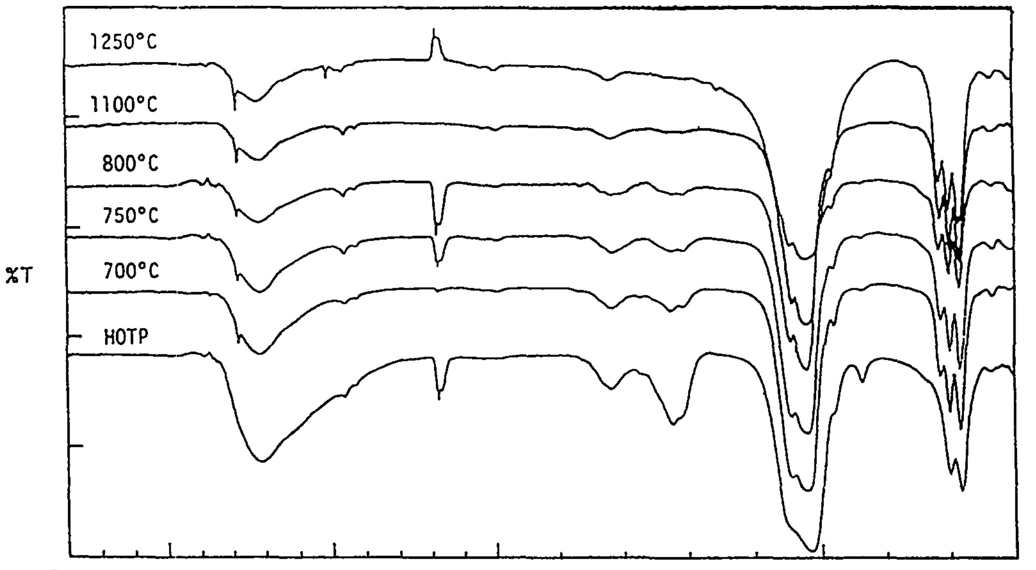

Fig. 2. IR spectra of mechano-chemically synthesized hydroxyapatite powders: starting powder and calcined powders at the most significant temperatures.

Table 2. Properties of HOTP powders prepared by mechano-chemical method, as obtained and after calcination (700°C, 1 h)

Calcination temperature (°C)	*Specific surface area ($m^2\ g^{-1}$)*	*Particle diameter (nm)*	*Distinguishable phases by XRD**
As prepared	168·8	< 12	a-HA
700	43·9	43	HA, β-TCP

*a-HA = Large band peaks of hydroxyapatite; HA = hydroxyapatite; β-TCP = β-tricalcium phosphate.

Table 3. Optimum synthetic conditions of production of hydroxyapatite H0TP powders by mechano-chemical method

Mechano-chemical reaction				
Apparatus	*Milling media*	*Milling time (h)*	*Reaction temperature*	*Powder content of slurry*
Teflon jar (70 × 100 mm)	Zirconia balls (15 mm, 800 g)	48 (280 r.p.m.)	Room temperature (25°C)	13 wt% $CaHPO_4 \cdot 2H_2O$ = 14·413 g $CaCO_3$ = 5·587 g H_2O = 150·000 g

Calcination conditions	
Calcination temperature (°C)	*Calcination time (h)*
700	1

we were interested in the mechanical properties of the ceramic bodies obtained using the proposed powders, an accurate determination of these was carried out to identify the specific conditions of preparation for the powders corresponding to the best results for mechanical resistance obtained on ceramized samples.

Among the systems examined, the best results were obtained using the raw material proportions and operative conditions reported in Table 3: the corresponding powder is that already coded H0TP in Table 1. The physical characteristics of H0TP powders are summarized in Table 2.

The density, mechanical strength and fracture toughness (Chevron-notched beam method) of samples produced by die pressing non-calcined H0TP powders are summarized in Table 4. Flexural strength and bulk density as a function of sintering temperature are also reported in Fig. 3. Shrinkage values at the different final firing temperatures are reported in Fig. 4.

Further experiments performed with the powders produced via the same mechano-chemical procedure, but employing porcelain jars according to the parameters of Table 1, surprisingly showed good results (Table 4; C-10). Since in the case of production of β-TCP in previous work,[8] the addition of Al_2O_3 and SiO_2 was demonstrated to produce strengthening effects on the obtained ceramics, the supposition was made that valuable results obtained with HA samples ground in porcelain jars

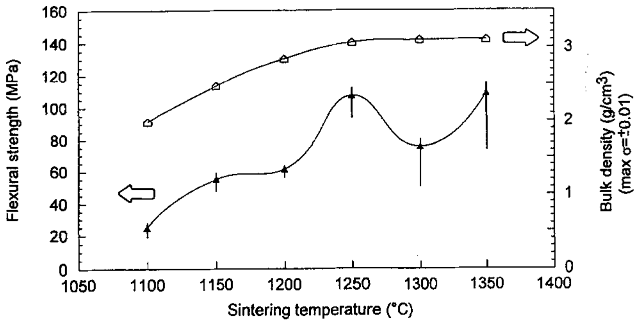

Fig. 3. Flexural strength and bulk density as a function of firing temperature.

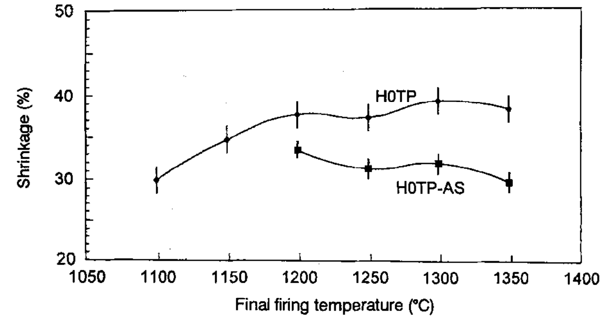

Fig. 4. Linear shrinkage trend during sintering of green bars made with H0TP and H0TP-AS by die pressing until indicated final firing temperature.

Table 4. Mechanical properties of mechano-chemically synthesized hydroxyapatite ceramics by die pressing

Powder code	*Optimum sintering temperature* °C	*Flexural strength** (MPa)	*Fracture toughness*[†] K_{IC} $MPa\ m^{1/2}$	*Bulk density* $g\ cm^{-3}$	*Distinguishable phases by XRD (proportional intensity)*[¶]
H0TP	1250	107·2	0·93	3·07	HA(80%), β-TCP(20%)
C-4	1300	35·3	—	2·41	HA(85%), β-TCP(15%)
C-10[‡]	1300	101·6	1·71	2·95	HA(34%), β-TCP(66%) c-ZrO_2 ,m-ZrO_2
H0TP-AS[§]	1250	130·4	1·64	3·04	HA(13%), β-TCP(X7%)

*Four-point bending method.

[†] Chevron-notched beam method.

[‡] Contamination with 15 wt% ZrO_2, 15 wt% SiO_2, 9 wt% Al_2O_3 and 1 wt% K_2O (from jar release).

[§] Deliberate addition of 2 wt% Al_2O_3 and 6 wt% SiO_2 (no crystalline traces of either visible by XRD).

[¶] HA = Hydroxyapatite; β-TCP = β-tricalcium phosphate; c-ZrO_2 = cubic zirconia; m-ZrO_2 = monoclinic zirconia.

could come from alumino-silicates released by the container during the milling. Therefore experiments were performed with the deliberate addition of Al_2O_3 (Alcoa A-16) and SiO_2 (Cab-O-Sil M-5, CABOT Co., Ravenna, Italy).

The mechanical properties measured for all these samples are shown in Table 4: the maximum value of flexural strength was found for a sintering temperature of 1250°C and for addition of 2 wt% Al_2O_3 and 6 wt% SiO_2. In this case, however, a body similar to 'vitreous porcelain' with poor mechanical properties is obtained at 1350°C, and a very large degree of transformation to β-TCP was observed. A marked reduction of mechanical properties is also shown by the samples made with H0TP powders fired above 1350°C.

4 Discussion

The variations in the mechanical properties of the obtained ceramics for the various operative conditions for manufacturing the powders mechanochemically is the basis of the supposition of a close cause and effect connection between starting conditions (and amount of defects) in the preparation of HA powder and final mechanical properties of the resulting ceramics. Among the possible variables that could play a role in determining the physical state under which the mechano-chemical process is carried out, there are the dimensions and the nature of the milling balls.

In the case of using Al_2O_3 balls as the grinding medium, $CaHPO_4{\cdot}2H_2O$ does not react with $CaCO_3$ (Table 1, D-l). The authors have formulated the hypothesis that with parity of dimensional (radius) distribution of the milling balls, the specific gravity of those made with Al_2O_3 (3·96) is not sufficient to reach the above mentioned threshold pressure that is reached when using ZrO_2 balls, with their higher value of density (6·05). Moreover, despite the large number of attempts to modify the dimensional distribution of Al_2O_3 balls, the expected reaction was never achieved. H0TP powder proved to be the most suitable for giving rise to ceramic bodies with high mechanical performance. Therefore the discussion deals mainly with this type of powder.

IR spectra analysis carried out on H0TP powder heated at various temperatures suggests that large levels of CO_3^{2-} groups are involved in the lattice of this defective HA, mainly instead of PO_4^{3-} at this site. This content of CO_3^{2-} inside HA strongly decreases towards 1250°C. With respect to OH^- groups, taking into account the limited decrease in intensity of their indicative peaks, it does not seem that they undergo an easy condensation process leading to H_2O elimination, at least up to 1250°C (Fig. 2).

The calcinated H0TP powder contains some fractions of β-TCP; nevertheless its Ca/P atomic ratio is always 1·67, not far from the theoretical value of pure stoichiometric HA, a value imposed by the chosen ratio of the raw materials in the synthesis of H0TP powders. Whereas an increasing trend in mechanical properties is exhibited by the ceramic samples fired at increasing temperatures, a loss of mechanical properties is observed in the range of firing temperature from 1250 to 1350°C, a change not justified by the evolution of the corresponding density of the obtained ceramics (Fig. 3). This mechanical 'failure', shows a minimum centred at 1300°C, when flexural strength values are larger for both lower and higher sintering temperatures. Such 'failure' cannot be ascribed to accidental or random causes because many series of measurements on many sets of samples confirm this trend. On the other hand it cannot be ascribed to a failure in the density of the material (Fig. 3). The same correlation could be identified in the trends of mechanical properties (Fig. 3) and shrinkage after firing (Fig. 4). One drawback is that the associated standard deviation (σ) hides the observed fluctuations of shrinkage with temperature.

To justify the surprising existence of this mechanical 'failure' in a temperature range where maximum values were expected, a variety of concomitant reliable physical circumstances can be considered: (a) intergranular phases; (b) grain growth; (c) diffusion effects; (d) release of gaseous components; (e) phase transformation of phosphate compounds; (f) chemical transformation of phosphate compounds; (g) a trend towards alignment and epitaxial rearrangement of crystallographic planes belonging to adjacent grains; (h) mobility of defects and vacancies; and (i) microporosity distribution. Those factors related to (a), (b), (d), (e) and (i) are certainly adverse to sintering, making the ceramic product brittle. Those reported in (g) and (h) tend, on the contrary, to favour hardness and mechanical toughness. With regard to the problem of diffusion effects (c), this can contribute to the stabilizing of the crystal lattice by arranging the different ionic species in energy levels as low as possible and helping intergranular phase reabsorption, which usually increases below 1300°C, while enormously decreasing above this.

The intergranular phase reabsorption is probably in equilibrium with the defects and vacancies of HA, which would justify the observed trend of the TCP/HA ratio of Fig. 1. This equilibrium is possible because of the intimate contact and distribution of the arising β-TCP that is largely expected to become part of the intergranular phase, just for this invoked mechanism. Control of the kinetics of this equilibrium is performed by the circumstances reported in points (g) and (h). For each temperature a 'best intergranular composition' exists. A contribution to the amount of microporosity and intergranular cavity reabsorption is also expected from the presence of this equilibrium which, on the other hand, is adversely influenced when other equilibria take place concerning, for example, phase transformations to other phosphate compounds and crystalline phases, mainly concerning the $\beta \rightarrow \alpha$ change of TCP (Table 5) that takes place starting from about 1180°C for pure β-TCP.[7]

Taking into account the non-negligible presence of β-TCP in heated synthesized powders, α-TCP could play a very important role in determining the mechanical 'failure' in the observed range of temperature (Fig. 3) due to the involved molecular volume increase, and consequent microcrack formation due to the back-transformation to β-TCP during cooling of the ceramic body of a fraction of α-TCP, that leads to some grain–grain detachments. The shift towards higher temperatures of formation of the first significative amount of α-TCP inside these samples (Table 5) is probably due to the interference brought about by the mentioned equilibrium.

By increasing the sintering temperature, the amount of intergranular phase decreases, while simultaneously the grains grow and the diffusion effects are enhanced. The decrease in intergranular phase and in diffusion phenomena tends to favour mechanical strength, while grain growth is adversely affected. Phenomena at points (g), (h) and (i) increase with sintering temperature and therefore mechanical strength is promoted more and more. Those at points (d), (e) and (f) play an adverse role at the temperatures of their respective occurrences.

Considering the involved phenomena overall, among the favourable and adverse ones, competition would arise, and one can think in terms of results characterized by one or more maximum and minimum in mechanical strength with respect to temperature. Since most phenomena bringing collapse of the mechanical properties (mainly phase and chemical transformations) occur in the temperature range between 1150 and 1300°C, the presence of the above mentioned mechanical 'failure' just inside this interval is justified. The corresponding temperature value (and those of the two related maxima) can vary according to the nature and morphology of the powders, and the specific HA composition and eventual presence of other concomitant compounds.

The formation of such a 'failure' (or discontinuity in the mechanical strength behaviour as a function of sintering temperature) is however by no means new, as there was observed, on different HA powders in the past, the existence of a maximum in mechanical resistance at 1230°C, followed by an inversion in this tendency at higher temperatures (at least up to 1250°C).[9] The temperature range between 1150 and 1250°C was then considered critical: it was stated that in such an interval the main part of the HA transformations occurred. The transformation hypotheses in the literature are manifold and forecast the formation of other calcium phosphates, mainly pyrophosphate and tricalcium phosphate.[10–12] Different types of pyrophosphates were proposed by Newesely,[13] while recent investigations[12] showed that HA at the highest temperatures decomposes with the formation of TCP and $Ca_4(PO_4)_2O$.

Moreover, the formation of oxyapatite was supposed, while others had mainly described the transformation as being a consequence of hydroxyl group release. In particular, it was hypothesized that in dehydration by hydroxylic condensation, the final material could be considered as an oxy-hydroxyapatite with vacancies related to hydroxyl sites.[14]

From firing experiments on various types of HA powders, it was observed that in such a temperature range unpredictable transformations can occur, often not revealable by XRD, and in some cases with the formation of different phases. This could depend first of all on HA stoichiometry (the content in replaced ions, CO_2, H_2O, etc.), and moreover on the presence, even in extremely reduced quantities, of other phosphate phases which could induce a trend towards one or another phosphate

Table 5. Per cent molar proportions of calcium phosphate compounds present inside the ceramic bodies made with HOTP powders at different firing temperatures, after cooling at room temperature

Phase	*Firing temperature (°C)*					
*(mol%)**	*1100*	*1150*	*1200*	*1250*	*1300*	*1350*
HA	85	85	83	80	76	73
β-TCP	15	15	17	20	20	20
α-TCP	0	0	0	0	4	7

*HA = Hydroxyapatite; β-TCP = β-tricalcium phosphate; α-TCP = α-tricalcium phosphate.

species, to be formed in the transformation. Consequently physical and chemical parameters and conditions are important in imprinting on the starting powders the physico-chemical characteristics that greatly influence the obtainable sintered products. Moreover, an investigation performed by some of the authors on commercially available HA powders,[15] showed evidence that many HA 'raw' materials contain, in general, 1–5% of $Ca_2P_2O_7$ in crystalline phase, easily disclosed by XRD. The presence of pyrophosphate can induce the reaction:

$$P_2O_7^{4-} + 2OH^- \text{ (from HA dehydroxylation)} \rightarrow 2PO_4^{3-} + H_2O$$

with subsequent β-TCP formation, that can already occur at temperatures between 650 and 750°C.[16] On the other hand, defective HA that may contain HPO_4^{2-} can also undergo the following transformation:

$$2HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$$

which comes to the previous reaction and consequently represents a possible example of the above mentioned equilibrium between β-TCP and defects or vacancies of HA grains.

The dehydroxylation of HA already begins to take place in the temperature range 850–900°C. At lower temperatures it does not interfere with sintering, while at higher temperatures (above 1150°C) it hinders sintering and causes the decrease in density, flexural strength and hardness of the obtained sintered compact ceramics. Knoop hardness of sintered HA shows a maximum of ~2000 MPa near 1130°C, while at lower and higher temperatures it quickly falls to ~480 MPa.[17] Similar behaviour is exhibited by flexural strength (Fig. 3).

In the H0TP powders, prepared in the present work, large chemical transformations are not identified except that deducible from IR spectra, which should produce HA through a CO_2 releasing reaction, besides the parallel one of hydroxyl condensation. In previous work on β-TCP,[7] an optimum sintering temperature of β-TCP powders synthesized by a mechano-chemical method was decreased some 50–100°C lower than that of β-TCP powders obtained by another synthetic methods. But a similar effect was not found in powders synthesized in this work by the mechano-chemical method, in spite of the particle diameter of the grains of the powder being smaller than that of β-TCP. For samples of β-TCP calcined over 720°C, the absorption peaks of CO_3^{2-} completely disappeared.[6] On the other hand, even if the calcination temperature was increased above 800°C, these peaks remain in the case of HA powders. IR absorption peaks gradually tend to become sharper with increase in temperature, except for a broadening between 1100 and 1250°C, which clearly indicates lattice deformations in the calcined grain mass.

Experiments performed with Al_2O_3 and SiO_2 additions show that for particular relative proportions of these compounds, good mechanical results are obtained, partially due to the formation of aluminium phosphate (with satisfactory mechanical properties). No crystalline phases were observed by XRD analysis of compounds containing these two added oxides. The supposition that aluminium phosphate is involved comes from the literature.[8] However their presence widely shifts the above-mentioned equilibrium existing between β-TCP and defective HA, as shown by the resulting per cent proportion of these in Table 4 (H0TP-AS samples), compared to the untreated ones (H0TP samples). In this case a very high amount of β-TCP arises at the expense of HA, and evidently the additions play a different role with respect to that involved when the matrix is completely made up of β-TCP only.[8]

Everything considered, we can pick out the temperature of 1250°C as the best for sintering H0TP powders to obtain the maximum mechanical resistance. This temperature is the same for powders with additions of Al_2O_3 and SiO_2. The temperature of 1250°C is chosen to produce ceramic bodies since it was revealed to be the maximum limit before formation of α-TCP. The corresponding values of fracture toughness (K_{IC}) of ceramics made with H0TP powders are shown to be practically equal to that of ceramic samples prepared with conventional powders. The fracture toughness of ceramics made with H0TP-AS powders (containing Al_2O_3 and SiO_2) are shown to be higher, probably influenced by close cohesion between the matrix and foreign compound grains. Having ceramic materials with practically only a microcrack propagation step, from the K_{IC} value of ceramics coming from H0TP powders the time of resistance to cyclic loading should be expected to be equal to that of a HA ceramic prepared with conventional powders; whereas from the K_{IC} value of ceramics coming from H0TP-AS powders, longer times are expected.

5 Conclusions

This work has shown the feasibility of using powders produced by a mechano-chemical method to constitute HA-based bioceramics. The described procedure concerns a product that contains β-TCP in a proportion estimated at around 10–12 wt% (20–23 mol%). The obtained ceramic exhibits very good flexural strength. The presence of Al_2O_3 and

SiO_2 additives leads to an increase in the mechanical properties but at the same time to a complete transformation of the nature of the matrix from HA to β-TCP. All the transformations observed during firing suggest that originally powders of defective HA give rise to HA and β-TCP in equilibrium at every temperature.

The existence of a critical temperature range was confirmed, in which a whole range of transformation phenomena occur associated with a decrease in the mechanical properties for sintered bodies. On the basis of previous experiences too, it is possible to state that such a critical temperature interval is not really fixed, but exhibits a certain degree of variability depending on the chemical quality and physical characteristics of the powders and their thermal treatments. For samples obtained by pressing H0TP powders elaborated in this work and produced through a mechanochemical method, the above mentioned 'failure' was found at 1300°C (with adjacent maxima at 1250 and 1350°C). A number of factors can, theoretically, contribute to the presence of such an interval of temperatures in which an adverse trend of the mechanical properties is observed. Certainly important among these are the grain growth and the development of anisotropy, but the authors consider the $\beta \rightarrow \alpha$ phase transformation of TCP to represent the main contribution, as evidenced by XRD results. CO_2 and H_2O losses are practically negligible and should not cause any considerable modification in the HA lattice.

Acknowledgements

The authors wish to thank Dr Stefano Guicciardi for his kind help and interest in the mechanical measurements.

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