

Effects of powder stoichiometry on the sintering of β -tricalcium phosphate

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Abstract

The impact of weak stoichiometry variations on β -TCP sintering behaviour was studied. β -Tricalcium phosphate (β -TCP) powders were synthesised by chemical precipitation through aqueous solution of diammonium phosphate and calcium nitrate. Excess or deficiency of nitrate salt leads to compositions with Ca/P ratios below or over 1.5. These powders, calcined at various temperatures (800–950 °C), were shaped by slip casting process and sintered at 1100 °C. The microstructure, phase composition, specific surface area and density of powders and sintered compacts were analysed by SEM, XRD, FTIR, BET, Archimedes methods and dilatometry.

This study shows that the presence of calcium pyrophosphate or the hydroxyapatite phases affects considerably the physical characteristics of the β -TCP powders and in particular specific surface area and consequently their sinterability.

A precise determination of the β -TCP chemical composition after synthesis allows to adapt the calcination temperature of the raw powder in order to obtain a maximum densification of the compact. The beneficial role of small quantity of HA phase inside β -TCP powder on their sinterability was also shown in this work.

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1. Introduction

β -Tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ is frequently used as bone graft substitutes in many surgical fields like the orthopaedic, dental, plastic surgeries.^{1–3} Its chemical composition, near to the bone, confers to its excellent biocompatibility and osteointegration properties. Moreover, its high resorbability in the human biological environment allows a significant recolonisation of the operational site by advancing bone growth during the progressive degradation of this material.

TCP can exist under three polymorphs, such as: β -TCP stable below 1120 °C with a density equal to 3.07, α -TCP stable between 1120 and 1470 °C with a density equal to 2.86 and α' -TCP above 1470 °C. Generally, β -TCP densification is difficult because the low temperature of $\beta \rightarrow \alpha$ phase transformation does not permit the sintering to high temperature. Indeed, this phase transformation hinders the TCP densification⁴ and, on the other hand, induces micro-cracking of the sample due to the

material expansion generated by density mismatch between β and α phases.^{4,5} In order to solve this problem, the influence of doping agent in β -TCP as magnesia or calcium pyrophosphate on the transformation temperature of β -tricalcium phosphate to α -tricalcium phosphate was studied by various authors.^{4–8} The role of these additives is to increase this $\beta \rightarrow \alpha$ transition temperature and thus to improve the characteristics of material by a sintering at higher temperature.

However, few works in the literature relate the influence of very weak variations of stoichiometry on the β -TCP densification.

Many methods are used to synthesise the β -TCP.^{9–12} The most conventional is the precipitation in aqueous medium starting from $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ as raw materials. However, the synthesis of a pure β -TCP by this method requires a close control of many parameters such as, reaction pH, ripening time, temperature, stoichiometry of the raw materials. A light variation of these experimental parameters can generate drastic variations in composition of the final product and reveal the pyrophosphate calcium phase ($\text{Ca}_2\text{P}_2\text{O}_7$ or CPP) or the hydroxyapatite phase ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ or HA). Thus, a 1 wt.% excess of calcium nitrate causes the formation of about 10 wt.%

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hydroxyapatite in the synthesised powder. The fact that raw materials are never perfectly pure or chemically homogeneous and that it can undergo various reactions as hydration or sublimation show the difficulty to obtain a perfectly stoichiometric product.

In this context, the stoichiometry influence of β -TCP powder on its sinterability is significant to determine.

2. Experimental procedure

2.1. Synthesis and characterisation of β -TCP powder

β -TCP powder was prepared by aqueous precipitation technique using a diammonium phosphate solution $(\text{NH}_4)_2\text{HPO}_4$ (Carlo Erba, France) and a calcium nitrate solution $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Brenntag, France).

The solution pH was adjusted at a constant value of 6.5 by a continuous addition of ammonium hydroxide. Temperature was fixed to 30 °C and the solution was matured 24 h. After ripening, the solution was filtered and the precipitate dried at 80 °C. Powders obtained with this synthesis process exhibit a too high specific surface area ($>60 \text{ m}^2/\text{g}$) for being directly used in the shaping process. So, the precipitate was calcined at 950 °C to increase the average primary particle size. After this operation, the powder was ground to break up agglomerates formed during the calcination and to reduce the powder to its ultimate particle size. Indeed, these agglomerates confine a significant water portion and then induce an increasing of slurry viscosity which must be compensated by a reduction of volume fraction of particles.

This grinding step was carried out by a ball milling with in a HDPE milling jar and Y-PSZ grinding media. The grinding time was fixed to 3 h.

This process was used to synthesise stoichiometric β -TCP and TCP with variable Ca/P ratio, close to 1.5, obtained with a light excess or deficiency of calcium nitrate compound.

Ca/P ratios of β -TCP superior to 1.5 was determined by Powder X-Ray Diffraction analysis (Rigaku Miniflex).

This quantitative analysis was performed using the intensity ratio of lines $I_{\text{HA}(211)}/I_{\text{TCP}(0210)}$ in according to method of the proportioned additions.^{13,14} The XRD spectra were collected employing a step width of 0.02° with counting time fixed to 20 s under 30 kV and 15 mA exciting.

Infrared spectra of powders were recorded on a Fourier transform spectrometer (Jasco-FT/IR-460 Plus) for estimating the Ca/P ratio of precipitates inferior to 1.5. Peak area of band at 720 cm^{-1} attributed to pyrophosphate group and in particular at P–O–P bonding, was used to evaluate amount $\text{Ca}_2\text{P}_2\text{O}_7$ by the method of the proportioned additions.

Morphological evaluation of powders was performed by a Scanning Electron Microscope (Hitachi S-3500N).

Specific surface area of calcined and ground powders was recorded by the BET method (Micromeritics, Flow Sorb 3).

2.2. Slip preparation and ceramic manufacturing

TCP slurries with a fixed powder concentration of 65 wt.% were prepared in a suspending liquid such as water. In order to

enhance slip stability, a commercial organic defloculant (Darvanc, R.t.Vanderbilt. Co.) was introduced in amount 1.5 wt.% of TCP content. A quantity of binder (Duramax B1001, Rohm and Haas) equal to 1 wt.% of TCP content was added also to ensure that the resulting cast was strong enough to be handled. After a planetary milling during 1 h using agate grinding container and balls, the slip was poured into plaster mould in order to obtain cylindrical samples with 10 mm diameter and 25 mm height.

After drying, samples were sintered at 1100 °C during 3 h with a heating rate of 5 °C/min. The powder sinterability was evaluated by dilatometry and densimetry trials. Thermal expansion-shrinkage of powder compact was measured with dilatometer (Netzsch 402C) in air atmosphere. Measurements were performed with 10 °C/min heating rate up to 700 °C then heating rate was adjusted to 2 °C/min up to 1250 °C.

Density of sintered samples was determined by Archimedes' method using distilled water. The relative density was calculated from theoretical density of β -tricalcium phosphate as 3.07.

3. Results and discussion

3.1. XRD and IR spectra

XRD patterns and IR spectra of powders obtained with a Ca/P slight modification of the initial reagent were shown in Figs. 1 and 2. These graphs allowed to estimate the Ca/P ratio of precipitated powders and the amount of various crystalline phases (Table 1).

The amounts of initial reagents were selected after various trials in order to obtain final powders stoichiometric and slightly under and over stoichiometry. Difference between initial and final Ca/P ratio can be explained by: (1) stoichiometric defect of raw materials as chemical purity, water adsorption, etc.; (2) a slight variation of manufacturing process parameters, as working temperature, reaction pH, slurry stirring, weighing, etc.

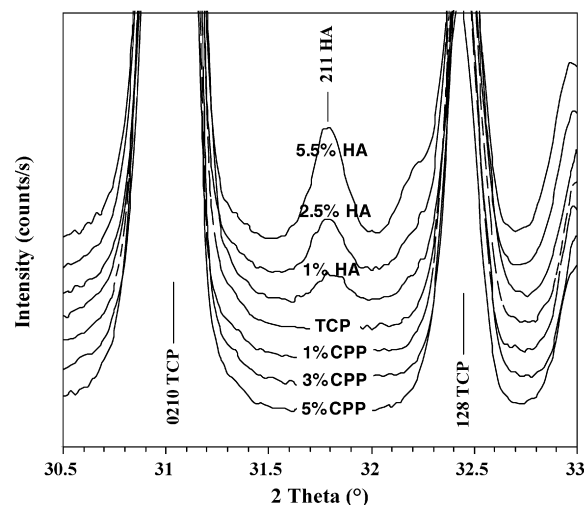


Fig. 1. XRD patterns of calcined powders at 950 °C for different Ca/P ratios.

Table 1
Final Ca/P ratios and phase compositions of calcium phosphate powders with different Ca/P ratios of initial reagents

Ca/p initial reagents	1.470	1.478	1.485	1.496	1.500	1.502	1.505
Ca/P final powders	1.470	1.482	1.494	1.500	1.501	1.504	1.509
wt.% Ca ₁₀ (PO ₄) ₆ (OH) ₂	–	–	–	–	1	2.5	5.5
wt.% Ca ₂ P ₂ O ₇	5	3	1	–	–	–	–

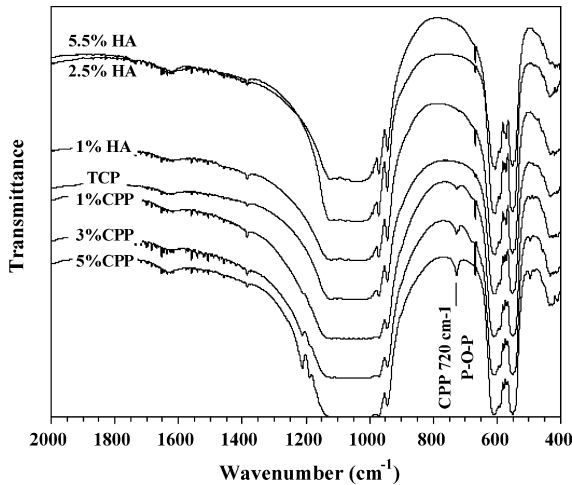


Fig. 2. IR spectra of calcined powders at 950 °C for different Ca/P ratios.

3.2. Sintering behaviour of TCP powders

Dilatometry analyses (Fig. 3) carried out on these different compositions showed distinct behaviours:

- Significant shrinkage, between 14 and 16%, appear for compositions enclosing weak amount of HA. Differential curves allowed to show that shrinkage starts at 780 °C with a maximum shrinkage rate at 1000 °C. After the shrinkage stage, a sharp peak become visible around 1100 °C in accordance with the expansion generated by the β → α transformation of tricalcium phosphate.

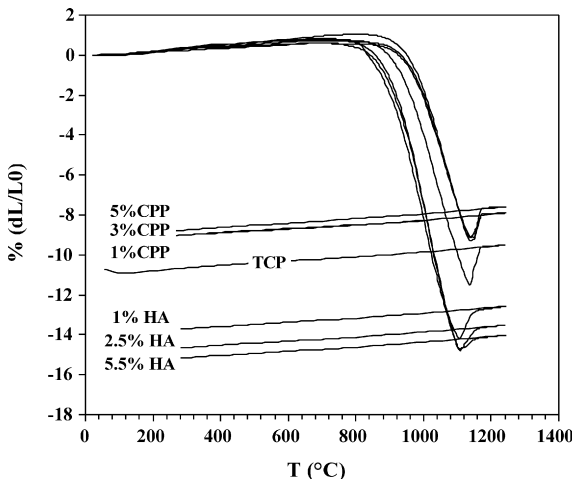


Fig. 3. Dilatometric analyses of calcined powders at 950 °C for different Ca/P ratios.

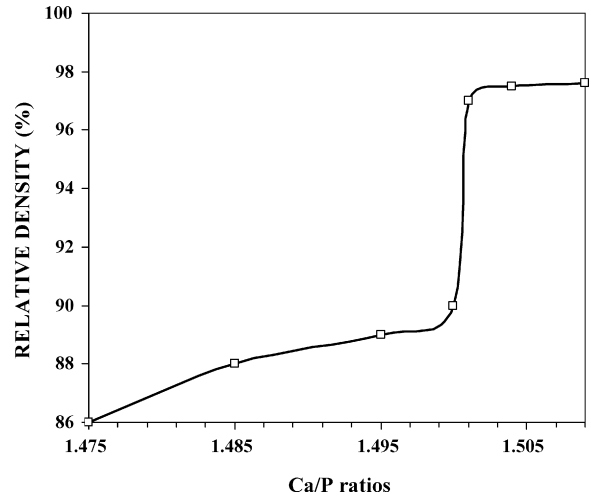


Fig. 4. Relative density of TCP powders calcined at 950 °C for different Ca/P ratios.

- For compositions with a Ca/P inferior to 1.5, shrinkage is lower than previously, around 10%. Densification starts at 880 °C with a maximum shrinkage rate at around 1050 °C.

The β → α transformation of TCP occurs at 1140 °C in the presence of pyrophosphate phase.

β-TCP stoichiometric exhibits an intermediate behaviour compared to the two previous ones.

Fig. 4 shows the evolution of material density for a varying Ca/P ratios and a sintering at 1100 °C during 3 h. Sintered compacts reach densities up to 97% of the theoretical density

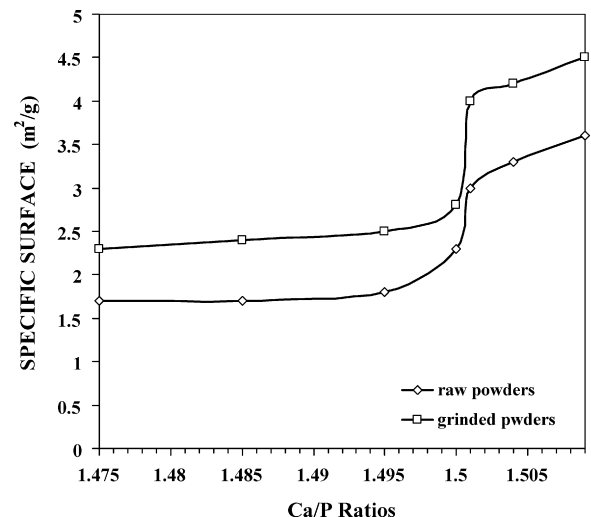


Fig. 5. Specific surface area of calcined TCP powders at 950 °C and grinded TCP powders for different Ca/P ratios.

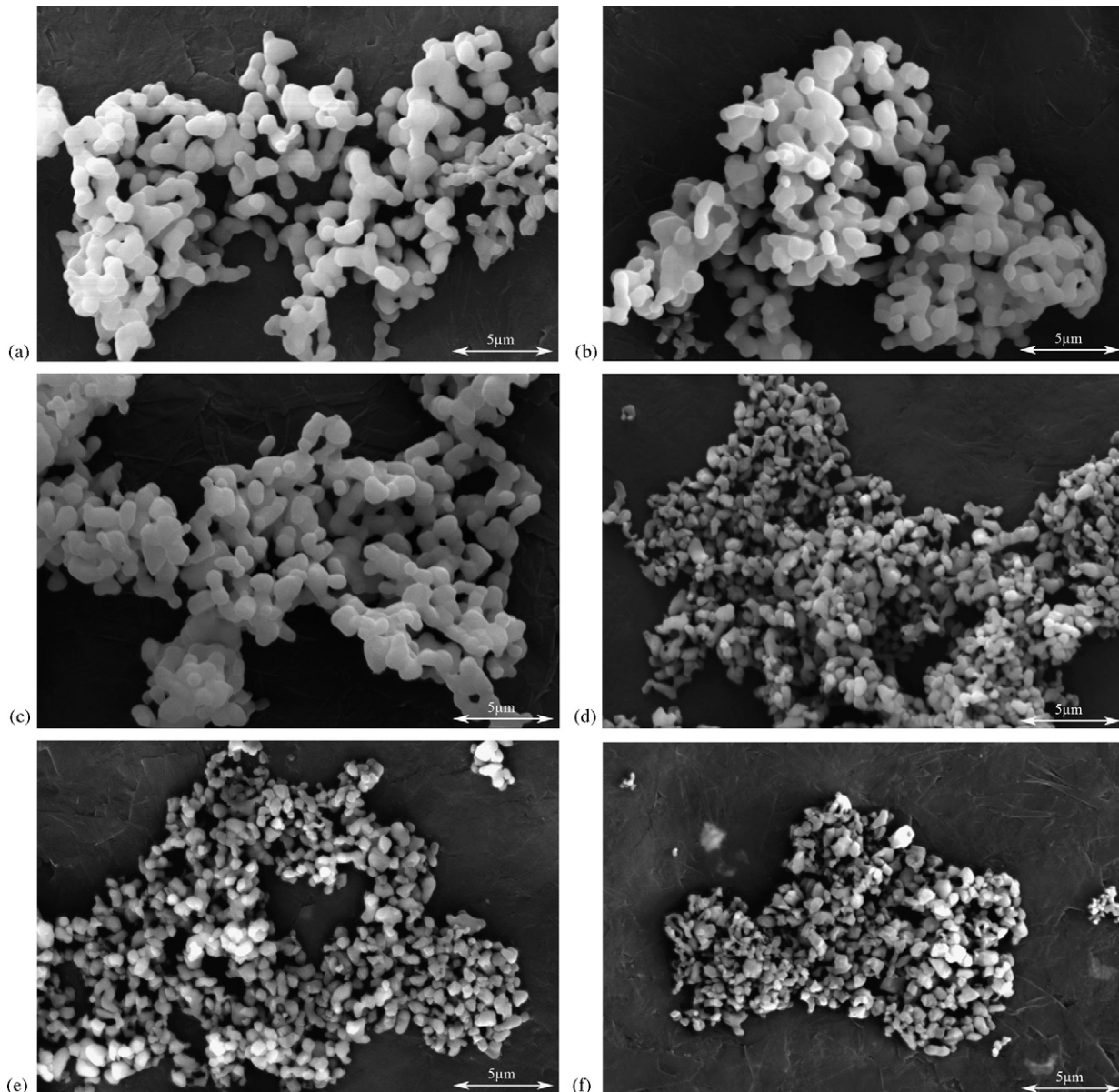


Fig. 6. SEM micrographs of TCP particles calcined at 950 °C with various Ca/P ratios: (a–c) 1, 3 and 5 wt.% $\text{Ca}_2\text{P}_2\text{O}_7$, respectively, and (d–f) 1, 2.5 and 5.5 wt.% $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, respectively.

when Ca/P ratio is superior to 1.5. However, relative density of material decreases with the Ca/P ratio reduction and values less than 89% are obtained with the samples containing the pyrophosphate phase. This density evolution according to Ca/P ratio corroborates results obtained with dilatometry analysis.

3.3. Powder granular properties

Specific surface area of calcined and ground TCP powders with different Ca/P ratios is shown in Fig. 5. This parameter increases with the rise of Ca/P ratio. For calcined powders, the values vary between 1.7 and 3.6 m²/g for compositions containing 5 wt.% of $\text{Ca}_2\text{P}_2\text{O}_7$ and 5.5 wt.% of HA, respectively. For ground powders, the values vary between 2.3 and 4.5 m²/g, respectively, for the same compositions.

In order to understand this specific surface evolution, the morphological features of calcined TCP powders at 950 °C with a varying Ca/P ratio were analysed by scanning electron microscopy. Fig. 6 shows that powders are constituted of agglomerated elementary particles due to diffusion bonding particles. Powders containing the pyrophosphate phase exhibit grains with a significant size which are strongly bonded ones with the others. For powders including the HA phase (Ca/P > 1.5), grain size is smaller and tends to decrease when HA concentration increases. These micrographs also show an abrupt morphological variation between over and under stoichiometric powders (1% HA and 1% CPP).

Pyrophosphate phase seems to help the bridging and thus the enlargement of the grain. Dilatometry and sintering trials were carried out from a pure pyrophosphate powder with a specific surface area equal to 4.5 m²/g. This powder was obtained after

calcination to 800 °C and grinding of calcium hydroxide phosphates or monetite. Results display that the powder compact densification starts at 650 °C with a relative density of material equal to 97% after a sintering to 850 °C during 3 h.

At the calcination temperature used (950 °C), the high reactivity of this phase could explain the coalescence and significant enlargement of the grain observed for the samples containing this phase. Concerning the samples with Ca/P ratio superior to 1.5, HA phase scattered in the matrix would act like an inhibitor of grain growth of TCP, owing to its weaker sinterability at the considered temperature.

These results show strong dependence between the powder stoichiometry and its sinterability at the calcination temperature (950 °C). So the influence of this temperature on the specific surface area and the sinterability of the powders were studied by using powders calcined at various temperatures, i.e., 900, 850, 800 °C for all chemical compositions.

The specific surface area was measured on powders ground during 3 h with a ball mill, optimised condition for obtaining a stable powders suspension.

Figs. 7 and 8, respectively, show the evolution of specific surface area and density of the samples at the various calcination temperatures.

For all the compositions, specific surface area and density increase when the calcination temperature decreases or when the Ca/P ratio increases. The significant variation of the density is again observed between the compositions just under and over stoichiometry for all calcination temperature.

For materials with a Ca/P ratio < 1.5, the values of density are low and calcination temperature lower than 800 °C would be necessary to obtain densities equivalent to materials including HA phase. However, for compositions with a Ca/P > 1.5, temperatures less than 800 °C lead to a significant increase of specific surface area and consequently would involve a viscosity increase of slurries due to increased particle–particle interactions.

Densities equal or higher than 99% are obtained for temperatures equal or lower than 850 °C when the samples contain HA

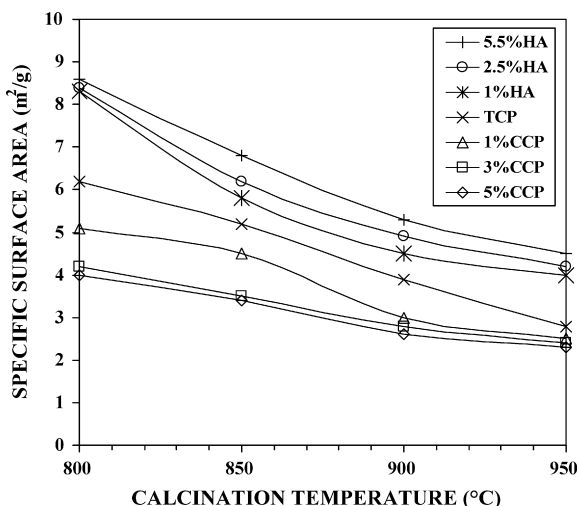


Fig. 7. Specific surface area of TCP powders calcined at various temperatures and with different Ca/P ratios.

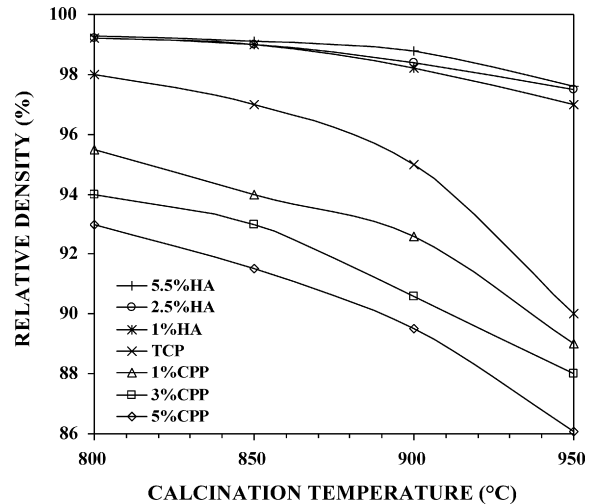


Fig. 8. Relative density of TCP powders calcined at various temperatures and with different Ca/P ratios.

phase. This behaviour is very narrowly related to the significant increase of the powder specific surface area.

Materials with a Ca/P = 1.5 ratio also show a positive evolution of the density with the reduction of calcination temperature. Densities of about 98% are obtained for calcination temperatures equal to 850 °C.

4. Conclusion

The synthesis method of β -TCP, based on precipitation in aqueous medium from $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reaction, leads frequently to very weak variations of the powder stoichiometry which have drastic consequences on the sintering behaviour. A precise characterisation of the powder, after synthesis, allows to adapt the calcination temperature according to the TCP stoichiometry.

However, this work shows that it is preferable to use compositions with a Ca/P ratio slightly higher than 1.5. Indeed, the presence of the hydroxyapatite phase inhibits the particle enlargement and thus, allows a better densification of material. For a calcination temperature of 850 °C and a sintering to 1100 °C, the presence of a small quantity of HA allows to reach densities equal or higher than 99% by preserving a value of specific surface area adapted to the development of stable low viscosity suspensions with high dry matter content.

Moreover, for biomaterial applications the presence of this phase is not inhibitory. Indeed standard ASTM F 1088-87¹⁵ establishes a minimum of β -TCP phase purity of 95% and thus, authorises a maximum percentage of 5% of hydroxyapatite in the composition of β -tricalcium phosphate.

The pyrophosphate phase has a harmful effect on the β -TCP sinterability due to an exaggerated enlargement of the particles during the calcination treatment. The $\text{Ca}_2\text{P}_2\text{O}_7$ presence requires calcination temperatures lower than 800 °C, and/or higher sintering temperatures. However, the use of higher temperatures for sintering causes an enlargement of grain of sintered material which is detrimental for the mechanical properties and

generates a significant cracking if $\beta \rightarrow \alpha$ transition temperature is exceeded.

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