CHARACTERISATION OF HYDROXYAPATITE-TRICALCIUM PHOSPHATE BIOCERAMICS ISSUED FROM CA-DEFICIENT HYDROXYAPATITE POWDERS: INFLUENCE OF Ca/P RATIO

SYLVIE RAYNAUD, ERIC CHAMPION, DIDIER BERNACHE-ASSOLLANT

Science des Procédés Céramiques et de Traitements de Surface, UMR 6638,
123, avenue Albert Thomas, 87060 Limoges, France.

Abstract Calcium deficient hydroxyapatite with Ca/P atomic ratio comprised between 1.5 and 1.667 were densified by hot pressing. Hot pressed powders were transformed into hydroxyapatite-tricalcium phosphate biphasic ceramics. After hot pressing at 1200°C, fracture strength remained below 100 MPa, this was explained by the allotropic transformation $\beta \rightarrow \alpha$ of TCP above 1150°C. Ceramics hot pressed at 1100°C had a fracture strength of 150 MPa when the composition contained between 8 wt% and 12 wt% of β -TCP. For lower or higher β -TCP content the strength dropped. This proved the necessity of a precise determination of Ca/P ratio. Quantitative X-ray diffraction analysis allowed a better precision than wet chemical analysis with deviations below 0.005 on Ca/P values.

INTRODUCTION

Several studies have been devoted to the synthesis of calcium deficient hydroxyapatite powders (Ca-dHAP) having a Ca/P atomic ratio comprised between 1.5 and 1.667, with the aim of elaborating hydroxyapatite-tricalcium phosphate (HAP-TCP) bioceramics.¹⁻⁴ Because reproducibility in hydroxyapatite synthesis and chemical characterisation have always been difficulties, relative deviations of 1% or 2% in the Ca/P value of synthesised calcium phosphates are often considered acceptable.^{5,6} But, such deviations may result in different ceramic materials after sintering.⁷

From this basis, the aim of our work is to point out the importance of a precise determination of Ca/P ratio of Ca-dHAP powders on the understanding of mechanical characteristics of densified ceramics issued from these powders.

EXPERIMENTAL PROCEDURE

Calcium phosphate powders of apatitic structure $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{HPO}_4)_x(\text{OH})_{2-x}$ with Ca/P atomic ratio ranging from 1.5 to 1.667 were synthesised from conventional precipitation method with $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ solutions.⁷ Because Ca-dHAP powders are transformed into HAP/ β -TCP biphasic mixture when heated in the temperature range 800°C-1100°C, the Ca/P ratio of initial powders can be determined using quantitative X-ray diffraction analysis (QXRD) of biphasic calcined mixtures.^{8,9} Powders were calcined at 1000°C and prepared according to the AFNOR NF S 94-066 standard. XRD patterns were registered on a θ/θ diffractometer (Siemens D5000) using $\text{CuK}\alpha$ radiation with a step size of 0.02° (2θ) and a step time of 19 seconds. For comparison classical wet methods were also performed (complexometry with EDTA for Ca and spectrophotometry for P).

Powders were hot pressed (H.P.) at 1100°C or 1200°C during 30 min under a 20 MPa compressive stress in an argon atmosphere. The relative density of hot pressed materials was determined by the Archimedean method in water. Sintered discs were cut into $20 \times 4 \times 3 \text{ mm}^3$ bars that were polished with a 3 μm diamond paste. Flexural strength was determined by 3 point bending of these bars with a 16 mm span and a crosshead speed of 0.2 mm min^{-1} . Fracture toughness was determined by Vickers indentation technique using a 19.6 N applied load. K_{IC} was calculated with Evans' equation.¹⁰

RESULTS AND DISCUSSION

XRD patterns of hot pressed ceramics (Figure 1) showed that at 1100°C, calcium phosphates were biphasic compounds containing HAP and β -TCP. α -TCP was present in the materials after heat treatment at 1200°C. Thus, the allotropic transformation $\beta\text{-TCP} \rightleftharpoons \alpha\text{-TCP}$, which occurs above 1150°C during heating, was not reversible during cooling to room temperature.

Characteristics of hot pressed ceramics are given in table 1. Pure TCP exhibited a much lower densification ratio than pure HAP and its presence modified the sintering kinetics of biphasic materials. Ceramics containing less than 30 wt% of β -TCP hot

pressed at 1100°C were nearly fully dense whereas residual porosity increased noticeably with increasing TCP content. After hot pressing at 1200°C, results were similar to that found at 1100°C and confirmed the low sinterability of TCP.

FIGURE 1. XRD patterns of calcium phosphate hot pressed at 1100°C and 1200°C (composition 77 wt% TCP and 23 wt% HAP, Ca/P = 1.536).

TABLE 1. Composition, densification ratio and flexural strength of hot pressed HAP/TCP biphasic ceramics.

Initial Ca/P molar ratio	TCP (wt%) after H.P.	Densification (%d _{th}) at 1100°C	$\sigma_{1100^{\circ}\text{C}}$ (MPa)	Densification (%d _{th}) at 1200°C	$\sigma_{1200^{\circ}\text{C}}$ (MPa)
1.667	0	97.8	76±25	98.9	98±20
1.663	2	99.8	122±20	99.9	76±10
1.653	8	99.1	152±20	98.0	98±15
1.646	12	98.2	149±30	96.2	55±25
1.617	28	99.0	127±20	98.8	84±40
1.536	77	85.4	90±10	92.5	30±5
1.500	100	83.8	46±10	86.0	18±4

Concerning the mechanical characteristics, the fracture toughness was almost constant whatever the composition might be with $K_{IC} = 1.0 \pm 0.2 \text{ MPa m}^{1/2}$ after hot pressing at 1100°C and $K_{IC} = 0.6 \pm 0.1 \text{ MPa m}^{1/2}$ at 1200°C . Conversely, the flexural strength of biphasic ceramics depended strongly on the composition referred to the initial Ca/P ratio. For dense materials hot pressed at 1100°C (containing less than 30 wt% of β -TCP), the fracture strength doubled from 75 MPa up to 150 MPa when the Ca/P ratio decreased from 1.667 to 1.653, i.e. from pure HAP to biphasic ceramics containing 8 wt% of β -TCP. Then, the strength decreased for lower Ca/P values. The low strength measured on ceramics containing high amounts of β -TCP (from 77 wt%) could be explained by the low densification ratio of these materials. After hot pressing at 1200°C , the fracture strength of ceramics remained always below 100 MPa. Moreover, an important dispersion in strength values was noted, showing a very poor reliability.

Finally, the high temperature treatment of 1200°C led to more brittle materials. The low mechanical characteristics of ceramics hot pressed at 1200°C could be explained by the transformation $\beta\text{-TCP} \Leftrightarrow \alpha\text{-TCP}$. The transformation is accompanied with an important variation of volume of about 7%. This variation should induce the appearance of residual stresses within the materials that are detrimental to the mechanical reliability. Residual stresses may even provoke the creation of microcracks which could account for the variability in strength and the decrease in toughness from $1 \text{ MPa m}^{1/2}$ at 1100°C down to $0.6 \text{ MPa m}^{1/2}$ at 1200°C . Therefore, the β -TCP to α -TCP transformation must be avoided to prevent a brittling of materials. This may be achieved providing sintering is performed at a temperature that does not exceed 1150°C . In this case, β -TCP may act as a mechanical reinforcement for HAP matrices with an important strengthening effect when present in low amount.

These results also show that a relative deviation as low as 1% in the experimental determination of Ca/P may constitute a serious drawback in bioceramics characterisation. The accuracy in the determination of this parameter is crucial. QXRD analysis of biphasic calcium phosphates (HAP/ β -TCP) calcined at 1000°C allowed us to establish that the ratio of two integrated intensities, each one corresponding to one of the two phases, was related with a good accuracy to phase proportions according to the following empirical equation :

$$R = \frac{I_{\text{phase 1}}}{I_{\text{phase 2}}} = \frac{A \times \text{weight\% phase 1}}{B - \text{weight\% phase 1}}$$

Diffraction peaks were chosen to minimise experimental errors and fitting discrepancies on empirical constants A and B. The most appropriated peaks corresponded to the reticular plane (0 2 10) for β -TCP phase and to the plane (2 1 0) for HAP when this phase is in major proportion or to the plane (2 1 1) for HAP phase when HAP is in minor proportion in the biphasic mixture. Therefore, two ratios of integrated intensities were used to the quantification :

$$R_1 = \frac{I_{\text{HAP (2 1 1)}}}{I_{\beta\text{-TCP (0 2 10)}}} ; R_2 = \frac{I_{\beta\text{-TCP (0 2 10)}}}{I_{\text{HAP (2 1 0)}}}$$

Figure 2 gives the relative deviation on Ca/P values calculated from QXRD analysis. The precision varied with the chemical composition. In the worst case (i.e. materials containing about 50 wt% of each phase), the method allowed to determinate Ca/P values with experimental errors below 0.4% whereas that obtained with wet methods was 2.5%. Nevertheless, complementary qualitative techniques such as infrared spectrometry appeared helpful to ensure the purity of initial Ca-dHAP powders before calcination for QXRD analysis.

FIGURE 2. Relative error on Ca/P atomic ratio determined from QXRD analysis.

CONCLUSION

HAP/TCP bioceramics having very different properties can be obtained inside a very small domain of composition. Therefore, a great attention must be given to experimental errors on the measurement of Ca/P ratio. QXRD analysis appears as a very accurate technique to determinate this parameter when Ca/P is comprised between 1.5 and 1.667. Tricalcium phosphate can reinforce hydroxyapatite matrices but the characteristics of biphasic calcium phosphate ceramics depend on sintering conditions. Sintering must be performed at a temperature below 1150°C to prevent the detrimental effect of TCP phase transformation. To this end, hot pressing appeared helpful.

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