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THERMAL DECOMPOSITION OF CARBONATED CALCIUM PHOSPHATE APATITES

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Abstract

The thermal stability of AB-type carbonated calcium phosphate apatites prepared by precipitation from aqueous media was studied. The behavior of powders was investigated using temperature programmed XRD, infrared spectroscopy and thermogravimetry. In N_2 atmosphere, two successive peaks of decarbonatation with maxima at about 700 and 950°C occurred. This behavior is explained by different substitution modes for carbonates in the apatite. The decarbonatation peaks were shifted to higher temperature under CO_2 (around 900 and 1150°C). The analysis of the thermal stability allowed further densification of carbonate apatite ceramics without important carbonate loss.

Keywords: bioceramics, carbonate apatites, thermal stability

Introduction

The main inorganic constituent of human bone has a crystalline structure and a composition very close to hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$. Mineral bone differs in composition from stoichiometric HA in that it contains several substituted ions either in the cationic or anionic sites of the apatite structure. Researches have demonstrated the presence of two types of carbonate (CO_3^{2-}) substitutions in the natural bone: CO_3^{2-} ions substitute partially phosphate ions (PO_4^{3-}) (B-type) and hydroxide ions (OH^-) (A-type).

The most employed method to prepare carbonate apatites is a precipitation reaction in aqueous media from the addition of a solution containing phosphate and carbonate salts into a solution of calcium salt [1]. This process leads to both A- and B-type carbonated apatite (AB-CO_3-Aps). Pure B-type carbonated apatites (B-CO_3-Aps) can have a complex vacancy structure and composition due to the substitution but also to possible other substitutions such as CO_3OH, HPO_4^{2-} or Na^+ or NH_4^+ depending on the synthesis conditions [1–5]. The thermal behavior of these powders can be influenced by the exact composition. Pure A-type carbonated apatites, that can also be prepared by heat treatment

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of HA for several hours in a CO_2 atmosphere between 800 and 1000°C [6], have a simple formula: $Ca_{10}(PO_4)_6(CO_3)_x(OH)_{2-2x}$, with $0 \leq x \leq 1$. Their thermal behavior is also well-known. The main difficulty encountered in the understanding of the thermal behavior of AB-type carbonate apatites comes from a possible interaction between A and B sites and from the multiple possible compositions that may change the behavior compared with pure A- or B-type compounds [4, 7].

The present work is a part of a study devoted to the synthesis and sintering of AB-type carbonated apatite ceramics with controlled carbonate content. It deals more particularly with the analysis of the thermal behavior of these AB-type powders under different atmospheres (air, N_2 CO_2) with the aim of defining conditions in view to further sintering of dense parts without decarbonatation.

Materials and methods

Powder synthesis

The powders were prepared by an aqueous precipitation method similar to that used for the synthesis of calcium deficient hydroxyapatite powders [8]. It consisted in the addition of a solution containing diammonium hydrogenophosphate ($(NH_4)_2 \cdot HPO_4$) (Aldrich, France) and ammonium hydrogenocarbonate ($(NH_4) \cdot HCO_3$) (Aldrich, France) into a reactor containing a calcium nitrate solution ($Ca(NO_3)_2 \cdot 4H_2O$) (Aldrich, France). The synthesis device was a fully automated apparatus. The addition rate was controlled using a peristaltic pump. The pH of the solution was maintained at the constant value of 8 by the addition of an ammonium hydroxide solution using a pH stat. The temperature was controlled and regulated at 90°C. The suspension was continuously stirred and refluxed. After total addition of the reagents, the suspension was ripened for 30 min. The Ca/P molar ratio of the initial reagents was 1.667. The carbonate substitution ratio in the apatite was controlled by the carbonate to phosphate (C/P) molar ratio of the initial reagents. Table 1 summarizes the different (C/P) ratios, sample notations and the resulting carbonate content in the powders determined from elementary analysis (CHN elemental analyzer 1106, Carlo Erba, Italy). Prior to this characterization the powders were heated in air at 400°C during 2 h in order to remove the synthesis residuals (mainly nitrates). This treatment does not affect the composition and crystalline structure of powders.

Table 1 Sample notations, molar ratio of reagents (C/P) and carbonate content in the powders

Notation	Molar ratio of reagents (C/P)	CO_3^{2-} content/mass%
HAP	0.000	0.0
C0125	0.125	3.3
C025	0.250	4.5
C05	0.500	5.5
C1	1.000	7.0

Powder characterization

Powder X-ray diffraction (XRD) patterns were recorded with CuK_α radiation on a $\theta/2\theta$ diffractometer (Siemens, Model D5000, Germany). The crystalline phases were identified from a comparison of the registered patterns with the ICSD powder diffraction files. Thermostructural evolution of powders was investigated from temperature programmed XRD (under CO_2 or N_2 gas flow) using a diffractometer fitted out with a high temperature furnace (Anton Paar HTK10, Pt heating sample holder) and an Elphyse position detector (aperture: 14°). Each pattern was recorded after a setting time of 10 min at the chosen temperature. The substitution type (A, B or AB-type) was determined by infrared spectroscopy on a Fourier transform spectrometer (Spectrum one, Perkin Elmer, USA) with a resolution of 2 cm^{-1}. Comparative analyses of spectra were possible after normalizing operation (each spectrum was normalized using the ν_3 PO_4^{3-} band at 1040 cm^{-1} considering that its intensity was constant whatever the composition might be) [9]. Thermogravimetry (TG) of powders was performed up to 1400°C in air, N_2 or CO_2 gas flow at the heating rate of 20°C min^{-1} (SDT 2960, TA Instruments, USA).

Results and discussion

Powder characterizations

XRD patterns (Fig. 1) of as synthesized powders at room temperature showed that they were single phased of apatitic structure. IR spectra of raw powders (Fig. 2) revealed the vibration bands of phosphate groups at 460, 560–600, 960 and 1020–1120 cm^{-1} and hydroxide groups at 630 and 3570 cm^{-1} that are characteristic of calcium phosphate apatites. A zoom on the ν_3 (Fig. 3a) and ν_2 (Fig. 3b) regions of carbonate vibrations showed that powders were of mixed type A and B. The bands at 878, 1455 and 1495 cm^{-1} were ascribed to carbonate ion vibrations in A sites [6, 10]. The existence of bands at 873, 1418 and 1455 cm^{-1} implied that carbonates were also present in B sites [11, 12]. The band at 1384 cm^{-1} corresponded to some remaining synthesis residuals (nitrates) after the 200°C treatment. There was no evidence for

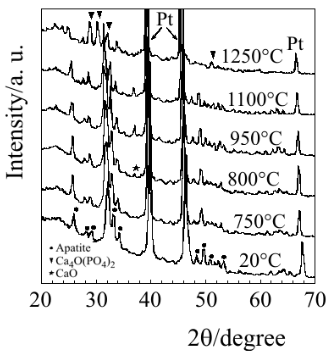

Fig. 1 Temperature programmed XRD patterns of powder C025 (N_2 atmosphere)

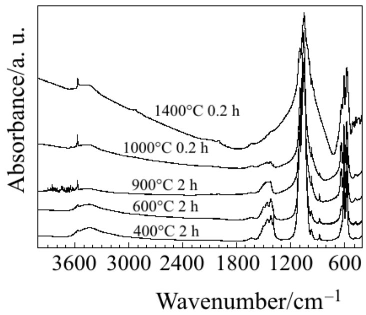

Fig. 2 FTIR spectra of C025 powder after calcination at different temperatures in air

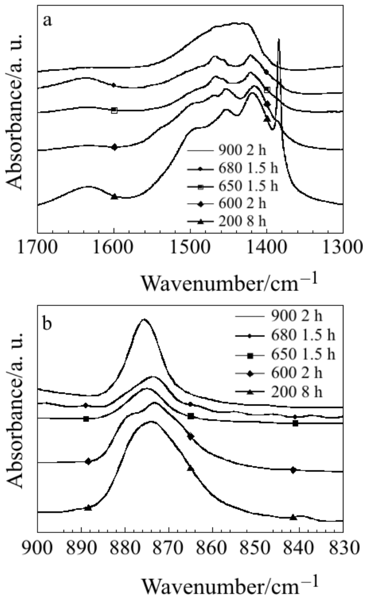

Fig. 3 FTIR spectra of the a – ν_3 region and b – ν_2 region of carbonate vibrations for powder C05 after calcination in air

any presence of hydrogenophosphate substitution; no infrared band of this group was detected. These results allow proposing a chemical formula that could be written in its most simplified form as:

$$Ca_{10-x}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x-2y}(CO_3)_y$$

Thermal behavior of powders

Figure 1 shows typical temperature programmed XRD patterns of carbonate apatite powders under N_2 atmosphere. The apatitic structure was preserved from room temperature up to 1250°C. At a temperature between 750 and 800°C, a second phase identified as CaO appeared. This phase is recognized to form from the decarbonatation of B-type CO_3-Aps [1]. The intensity of its diffraction peaks increased up to 1100°C. Then, at about

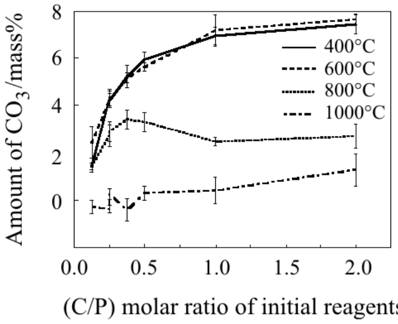

Fig. 4 CHN elementary analyses of powders calcined for 2 h in air

1250°C, CaO disappeared and tetracalcium phosphate monoxide $Ca_4O(PO_4)_2$ (TCPM) was formed. Conversely, when heated under CO_2 atmosphere neither crystalline change nor secondary phase formation was detected from room temperature up to 1250°C. IR spectra performed on powders heated at different temperatures in air (Figs 2, 3) showed the progressive disappearance of carbonate vibrations above 600°C. This result was confirmed by the elementary analyses of carbonate content of powders heated at different temperatures in air for 2 h (Fig. 4). No decarbonatation occurred up to 600°C, whereas only a third of the initial carbonates remained at 800°C. Then, they were nearly totally removed at 1000°C. Figures 5 and 6 give the plots of mass loss *vs.* the temperature and the derivative plots of thermogravimetry (DTG), respectively. The behavior of powders could be divided in four parts corresponding with the different peaks of gas releases:

I) 20–600°C: departure of adsorbed water and synthesis residuals (mainly nitrates, which IR peak at 1380 cm^{-1} had disappeared from 600°C).

II) 600–1050°C: carbonate losses. Two kinetics of carbonate departure were identified. The first one began at around 550°C for the lowest carbonate content in the initial apatite (C0125) and shifted to higher temperatures with the increase of this carbonate content to reach 600°C for C1 powder. Therefore, increasing the carbonatation of the apatite stabilizes it. The second departure had a maximum at about 950°C. The mass loss registered in this domain was between 4 and 8%. These values are slightly higher than that determined for the carbonate content of the initial powders. But, in this temperature range, the dehydroxylation of the A sites of the apatites with the formation of oxyhydroxyapatite and water departure also began. The related mass loss is included in the above mentioned total.

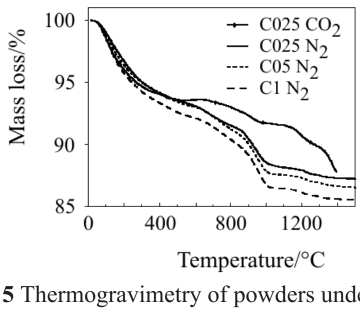

Fig. 5 Thermogravimetry of powders under N_2 or CO_2

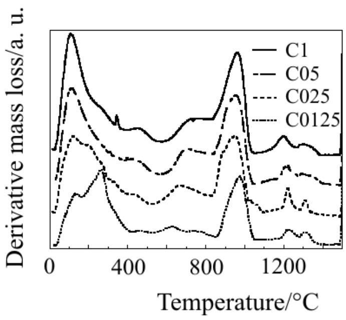

Fig. 6 Derivative plots of thermogravimetry curves under N_2

In this temperature range, the attribution of the two distinguished CO_2 departures to A or B sites decarbonatation seems difficult. But, IR spectra would indicate a decrease of A site carbonates with increasing temperature from 600°C with the decrease of the A carbonate band at 878 cm^{-1} (Fig. 3b). The increase of the hydroxide bands after cooling in air would agree with this hypothesis (Fig. 2). The formation of CaO above 750°C, temperature that corresponds with the beginning of the second peak of gas release would indicate that it relates to the carbonates of B sites. Nevertheless, care must be taken because of possible low kinetics effects and induced shifting in the detection of the different phenomena due to the procedures of temperature programmed experiments. XRD pattern registered on powder of composition C05 after isothermal calcination at 650°C for 15 h in air, temperature that corresponded with the first mass loss peak registered by TG, showed that the powder remained single phased. No formation of CaO was detected. But, this second phase was present in the same powder after 15 h of calcination at 680°C, which could make the previous interpretations ambiguous though this formation should rather be attributed to the beginning of the second peak of mass loss under isothermal conditions.

The assumption that carbonate ions substituted in A sites of the apatite would be released at lower temperature than those substituted in B sites of AB-type CO_3-Aps could appear somewhat controversial in comparison with the literature. Indeed, it is generally considered that carbonate in A sites are thermally more stable than those contained in B sites. This is the case for pure A-type CO_3-Aps that are known to be stable up to 900°C [13] whereas pure B-type CO_3-Aps are stable up to only 700°C [1]. Nevertheless, A-type CO_3-Aps were also found to decarbonate at much lower temperature depending on their preparation conditions [14]. More, small differences in the apatite chemical composition may contribute to important changes in the thermal stability. Some authors [4, 15, 16] deal with the migration of carbonate from B sites to A sites from about 400°C, but in the presence of additional hydrogenophosphates in B sites. The proposed mechanism is a reaction between carbonate and hydrogenophosphate ions in B sites that forms CO_2. Then this CO_2 migrates through the apatite channels, therefore through A sites, according to:

$$2HPO_4^{2-}+CO_3^{2-}\rightarrow CO_2+2PO_4^{3-}+H_2O$$

$$CO_2+2OH^-\rightarrow H_2O+CO_3^{2-}$$

The presence of fluoride ions in A sites also decreases the temperature of decarbonatation of B-type CO_3-Aps down to 500°C [7].

Finally, the thermal stability of CO_3-Aps depends strongly on their exact chemical composition and it appears that the lower thermal stability of carbonates in B sites than that of carbonates in A sites is issued from the presence of other substituted ions in the apatite, which is not the case of the CO_3-Aps used in the present study.

III) Around 1250°C: the DTG peak was attributed to water release associated with the reaction between the oxyhydroxyapatite and CaO with the disappearance of CaO (minor specie) and formation of TCPM (observed on XRD patterns, Fig. 1) according to the following reaction:

$$Ca_{10}(PO_4)_6(OH)_{2-2x}O_x+2CaO \rightarrow 3Ca_4O(PO_4)_2+(1-x)H_2O$$

IV) Around 1300°C: the last TG peak was associated with the decomposition of the remaining oxyhydoxyapatite into tricalcium phosphate and TCPM as [8]:

$$Ca_{10}(PO_4)_6(OH)_{2-2x}O_x \rightarrow 2Ca_3(PO_4)_2+Ca_4O(PO_4)_2+(1-x)H_2O$$

A typical plot of thermogravimetry performed in CO_2 flowing gas is given in Fig. 5. Compared with N_2 atmosphere, the total mass loss at 1400°C was similar but the mass losses associated with the departure of carbonates (domain III) occurred at higher temperatures. The first carbonate loss occurred between 600 and 1000°C with a maximum at about 950°C. After this first departure only a third of initial carbonates was removed. The second carbonate release began at 1100°C and proceeded up to 1300°C.

This important stabilization of carbonate ions in comparison with the behavior in inert atmosphere allowed the densification of ceramic materials by sintering at low temperature under dry CO_2 atmosphere. After sintering for 2 h at 950°C, pellets of C1 composition exhibited a density of 2.79 with an open porosity below 9%. A very recent study concluded to a similar behavior [17], a carbonate apatite being densified at a temperature approximately 200°C below that required to sinter stoichiometric hydroxyapatite.

Sintering at higher temperature led to a decrease of the density. IR Spectra of ground pellets sintered under CO_2 for 2 h at 950°C is given in Fig. 7. Evidence ex-

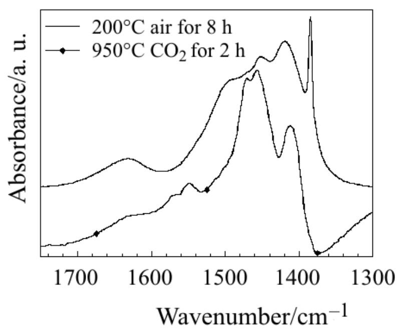

Fig. 7 FTIR spectra of the ν_3 region of carbonate vibrations for powder C1 after calcination at 200°C and powdered ceramics sintered under CO_2

isted for the presence of carbonates in both A and B sites. Some changes in the relative peaks intensities could be observed after this thermal treatment. A peak at 1555 cm^{-1} that was not directly observable in powders heated in air or N_2 appeared clearly. It could be attributed to A-type carbonates. In comparison with the band of B-type carbonate at 1410, the bands at 1470 cm^{-1} (A-type) and 1455 cm^{-1} (A and B-type) seemed more intense after the heat treatment under CO_2 at 950°C. This would indicate a light carbonatation of A sites during the sintering.

Conclusions

Mixed AB-type carbonate apatite powders with variable carbonate content were prepared by precipitation method in aqueous media. CO_3-Aps powders are thermally unstable. The decarbonatation starts from about 600°C and proceeds in two steps. Considering the whole experimental results, the hypothesis retained to explain the thermal behavior of mixed AB-type CO_3-Aps in air or inert atmosphere is that carbonate ions contained in the A sites of the apatite would begin to be removed at lower temperature than those substituted in B sites. The stabilization of carbonate at higher temperatures under CO_2 atmosphere allows the sintering of AB-type CO_3-Aps ceramics at very low temperature under CO_2 without important decarbonatation of B sites. From these last bases, a complete analysis of the densification process of these AB-type carbonate apatites of different compositions under controlled atmospheres, in particular in dry CO_2 and CO_2/H_2O mixtures, is under progress with the aim of determining the sintering mechanisms.

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