

DEVELOPMENT AND CHARACTERIZATION OF HYDROXYAPATITE FOR BONE USE

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ABSTRACT

The objective of this work is the elaboration of a biomaterial Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), by a synthetic method of precipitation, ($\text{CaCl}_2, 2\text{H}_2\text{O}$) as source of calcium and ($\text{Na}_2\text{HPO}_4, 12\text{H}_2\text{O}$) as a source of phosphate. After preparation, the powder was calcined at 900 °C for 90 minutes at a speed of 10 °C / min and compacted into pellets 12 mm in diameter and 2 mm thick. Sintered powder at different temperatures (1000°C, 1100 °C, 1200 °C, and 1300 °C). In order to study the effect of sintering temperature on the microstructure, the physical and morphological properties of the elaborated hydroxyapatite, the density, the porosity, X-ray diffraction (DRX) and the scanning electron microscopy (SEM) were used for the characterization of the powder. The density decreases with the increase of the porosity, in fact the sample densifies easily when the porosity is lower.

Keywords: Hydroxyapatite, SEM, DRX, Porosity, Density.

1. INTRODUCTION

Biomaterials used as implants or fillers are attracting increasing interest because of their frequent use in reconstructive surgery or orthopedic surgery. They represent an alternative to autografts (tissue samples from the individual), allografts (tissue removal from an individual of the same living or dead species) and xenografts (tissue samples from a different species). During bone loss, bone substitute materials are used to facilitate the ossification of a defect that cannot heal without external input. At the crossroads of multiple scientific disciplines (materials science, mechanics, chemistry, biology), the field of biomaterials is subject to important social and economic issues [1,2].

Hydroxyapatite (HA), with chemical composition $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a biocompatible and bioactive material with a crystal structure similar to biological apatite that can be found in hard tissues such as teeth and bones. It has been widely used in orthopedics and dentistry because of its close biocompatibility with the human body and its good integration with bones. In addition, it offers various shaping possibilities, since it is possible to manufacture powder, coatings, dense bodies and porous bodies [3].

Therefore, it has been suggested that HA is the best substitute for bone. HA is a ceramic material having low mechanical properties, in particular low tensile strength and fracture toughness. Its application is limited to those parts of the human body that are subjected to reduced mechanical stress or compressive stress only [4].

Hydroxyapatite is composed of ions (mainly Ca_2^+ and PO_4^{3-}) that occur naturally in tissues and, therefore, hydroxyapatite does not possess the biotoxic properties and can be safely introduced to the human body [5-6].

In this study we present the structural and morphological properties of a hydroxyapatite elaborated by chemical precipitation, as well as the effect of sintering temperature on density.

2. EXPERIMENTAL

2.1 Materials

HA, with stoichiometry ratio $\text{Ca}/\text{P} = 1.6$, was synthesized by chemical wet method from (1) hydrated calcium chloride ($\text{CaCl}_2, 12\text{H}_2\text{O}$) as a source of calcium and (2) dehydrated di-sodium hydrogen phosphate ($\text{HNa}_2\text{PO}_4, 2\text{H}_2\text{O}$) as a source of phosphate. Stirring was carried out at 80 °C. With a speed of 300 rpm, a flow

rate of 5ml/min and finally a duration time of 1 hour according to the following diagram (fig.1), obtained powder was heated at 900°C and washed in order to purified it from any organic residues.

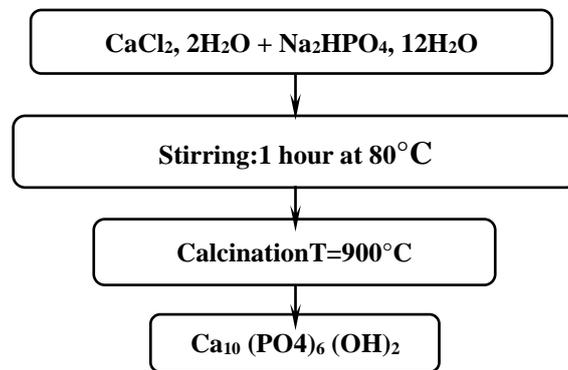


Figure 1. Synthesis steps.

2.2 Sintering treatment

The powder compressed into 12 mm diameter and 2 mm thick pellets in a hydraulic press of the SPECAC 25T Advanced Materials Research Unit (URMA / CRTI). The sintering temperatures are 1000°C, 1100°C, 1200°C and 1300°C at a speed of 10 °C / min (fig. 2).

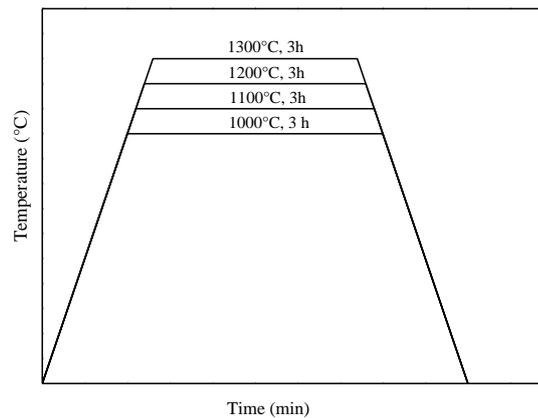


Figure 2. Sintering cycle.

2.3 Microstructural analysis

The X-ray diffraction analysis is carried out on a Rigaku spectrometer of the Advanced Materials Research Unit (URMA/CRTI). The scan rate is 2°/min at 2000 cycles using CuK α radiation with a wavelength $\lambda = 0.154056$ nm.

2.4 Density and porosity

Density and porosity were measured on a Micromeritics Helium Pycnometer *the AccuPyc II 1340 Gas Pycnometer* (fig. 3), in Applied Research Unit (URASM/CRTI), which determines the effective density of a powder or bulk material according to the measurement of its volume. During the test, the pressure variation leads to calculating the volume of the sample from Mariotte's law (Eq. 1):

$$V_{\text{pellet}} = \frac{V_{\text{cell}} - V_{\text{expansion}}}{\frac{P_1 - P_1}{P_1 - P_a} - 1} \quad (1)$$

With:

V_{cell} : cell volume

$V_{expansion}$: expanded volume

P_1 : Pressure in the sample chamber only

P_a : Pressure after expansion



Figure 3. Micromeritics AccuPyc II 1340 Gas Pycnometer.

2.5 Morphological analysis

The observation of the powder morphology is carried out using a ZEISS Gemini SEM 300 scanning electron microscope. Work tension is within the interval 5 to 30 kV, allows a magnification up to 30 thousand times.

RESULTS

The obtained powder is the hydroxyapatite as confirmed in the work of Alimi et al [7]. In figure 4 the spectra of the sintered pellets are presented. We can see that there is no change in the phase's composition with the 4 sintering temperatures.

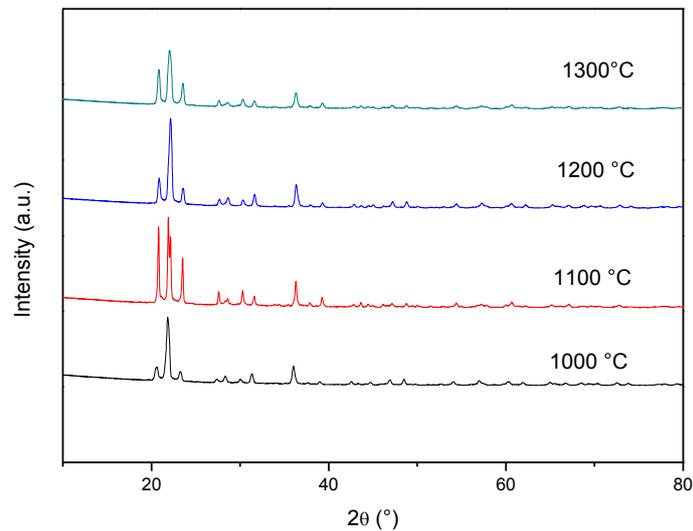


Figure 4. DRX spectra for sintered samples

For measurements of density and porosity (fig. 5, 6), the results obtained are summarized in Tables 1. The theoretical density of hydroxyapatite is 3.16 g/cm^3 [8], while the measured density of our powder is about 2.3 g/cm^3 .

The effective density evolves slightly with the increase of the sintering temperature; indeed, it corresponds to the density of the crystalline phase. On the other hand, the bulk density decreases with the increase of the porosity, the sample densifies easily when the porosity is lower [9].

Table1. Density measurement and the porosity of hydroxyapatite

Sintering temperatur	effective density	Bulk density	Porosity (%)
1000°C	2.311	2.303	56.54
1100°C	2.308	2.296	56.53
1200°C	2.307	2.29	56.23
1300°C	2.305	2.281	56.11

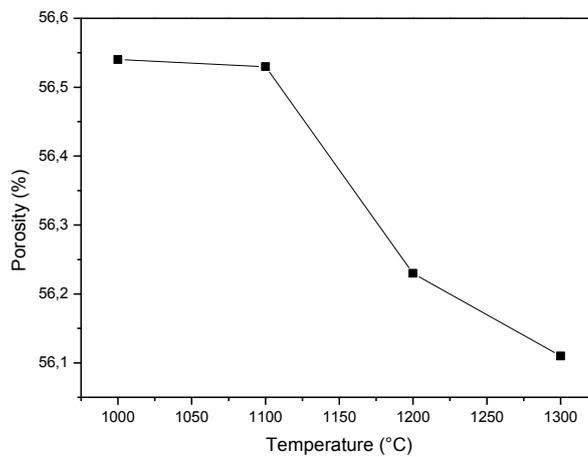


Figure 5. Porosity evolution with sintering temperature

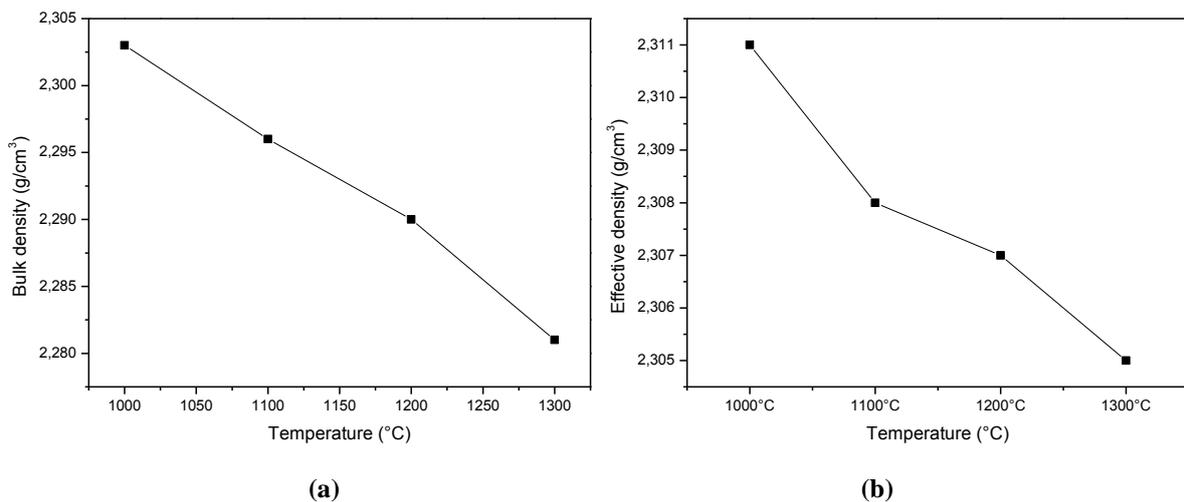


Figure 6. Variation density with sintering temperature (a) Bulk and (b) effective.

The microstructure of the HA powder before sintering, observed by SEM, is presented in figure7. We note that there are two distinct morphologies observed: spherical and lamellar shape. The size of the lamellae exceeds 3 μm whereas the spheres do not exceed 1 μm .

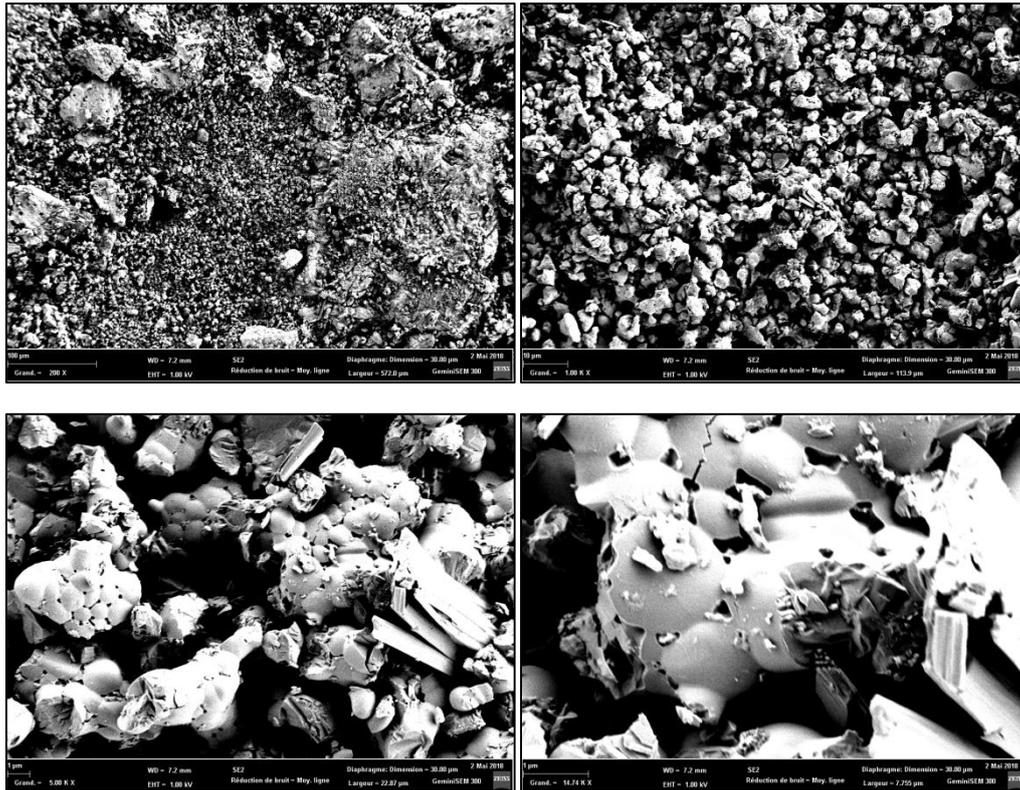


Figure7. SEM micrographs of obtained powder with different scales.

Conclusion

In this study, effect of sintering temperatures on porosity of synthetic HA were studied using X-ray diffraction and density measurements. It was found that synthesis HA is stable in the range of sintering temperatures studied (1000-1300 °C).

The increase of density with sintering temperature is very insignificant, about 2 %. Porosity decrease with increasing sintering temperature; the decrease is about 7% in case of 1300°C.

NOMENCLATURE

HA	Hydroxyapatite
ρ	Density
V_{cell}	Cell volume
$V_{expansion}$	Expanded volume
P_1	Pressure in the sample chamber only
P_a	Pressure after expansion

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