Study of the Microstructural and Mechanical Properties of a Phosphocalcic Bone Substitute

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Abstract. The choice of calcium phosphate materials in reconstructive surgery is justified by the surprising similarities between the composition of these materials and that of the bone. Among a multitude of bone substitutes, hydroxyapatite of chemical composition Ca₁₀(PO₄)₆(OH)₂ is the material most similar to natural apatites. In this study, hydroxyapatite was developed using the wet precipitation method from hydrated calcium chloride (CaCl₂.12H₂O) as a source of calcium and di-sodium hydrogen phosphate dihydrate (HNa₂PO₄.2H₂O) as a source of phosphate. Vickers Microhardness tests and XRD analyzes were used for the characterization of the synthesized material. The mechanical properties namely HV, σe, and σr, KIC and microstructural like cristallite size Dhkl and degree of cristallinity Xc, were discussed according to the temperatures of the heat treatments. Two temperatures were chosen 900 and 1200°C. From the results obtained, it is obvious that the variation of the different properties studied correlates with the temperature of the heat treatment.

INTRODUCTION

The aging of populations and the increased life expectancy give rise to an insistent call for bone and synthetic grafts that can essentially replace, repair or regenerate lost bones. In medical and dental fields, the main application of this material is as bone graft, where Hydroxyapatite is used to promote the growth of new bone [1]. Phosphocalcic bone substitutes are increasingly used in human therapeutics because of their microbiological safety and effectiveness [2]. Calcium phosphate ceramics are dense and porous bioactive materials, which belong to the family of bone substitute biomaterials, thanks to their particular physicochemical, biological characteristics and biocompatibility [3,4].

Calcium phosphates contribute to the formation of the major mineral phase of hard tissues, their dissolution properties are strongly related with their physicochemical characteristics, and the Ca/P molar ratio, crystallographic structure, pH and specific surface. In the various existing combinations of these calcium phosphates, the two ceramics that had the most attention are hydroxyapatite (HA), and tricalcium phosphate (Ca₃(PO₄)₂), also called TCP, as well as their mixtures [5]. Hydroxyapatite HA is the main mineral constituent of bone tissue. HA is
biocompatible with the human organism and is able to integrate biologically into bone tissue [6]. The structural, morphological and chemical properties of synthetic HA can be controlled by changing the technique and the environments of synthesis. Conventional procedures for HA powder synthesis cover direct precipitation, hydrothermal techniques, hydrolysis of supplementary calcium phosphates, like solid state reactions and mechanochemical approaches [7]. Wet precipitation is one of the greatest generally used techniques. Chemical reactions take place between calcium and phosphorus ions below a specific pH and temperature of the mixture. The precipitated powder is usually calcined at 400-600°C or even at higher temperature to get a stoichiometric, apatitic structure [8].

The biological behavior of bioactive ceramic bone substitutes is quite well known. It appears that their characterization should not be limited to their biological properties alone. Due to the complexity of the mechanical stresses exerted, the mechanical properties of these bioceramics must be studied and mastered as well. Their excessive fragility and their average mechanical properties can be considered as disadvantages to their use in parts highly exposed to mechanical stresses [9]. In articular systems, exhibiting surfaces in complex relative motion, the surface properties (hardness, elasticity, friction, roughness) have as important a role as volume properties, at the interface between prosthetic parts or at the interface with bone and its binding, and in contact with the different body physiological fluids. The evaluation of the mechanical strength of these implants depends on the activity of the wearer, the muscle tone, the postures, the quality of the bone and its link with the implant [10].

Rupture of ceramics is usually initiated by pre-existing defects or anomalies. The characterization of the mechanical properties is an important step to validate the accuracy of the production process as well as the essential properties of hydroxyapatite. The objective of this study was the characterization of hydroxyapatite powders synthesis by wet precipitation method. The heat treated powders were characterized by X-ray diffraction in order to identify the phase composition and crystallinity of the calcium phosphate compounds. Also this study would make possible to determine the effect of the sintering temperature on some mechanical properties namely the microhardness, the rigidity and the tenacity of the synthesized hydroxyapatite.

Experimental Work

Preparation of the Hydroxyapatite Powder

The aqueous precipitation synthesis method was used from hydrated calcium chloride (CaCl₂, 12H₂O) as a source of calcium and di-sodium hydrogen phosphate dihydrate (HNa₂PO₄, 2H₂O) as a source of phosphate. While respecting a molar stoichiometry Ca/P=10/6. The chemical reaction was proceeded under a PH 9, a reaction temperature equal to 80°C, a stirring speed 300rpm, a flow rate 5ml/min and finally a holding time close to 60min. The synthesized powder was subsequently put into the form of pressed pellets of diameter equal to 10mm and thickness <3.5mm. The hydroxyapatite pellets were then heated at temperatures of 900°C and 1200°C. According to the literature this last temperature is ideal to obtain a perfectly crystalline hydroxyapatite [8].

Characterization

XRD

The identification of the crystalline phases present in the elaborated powders was carried out by X-ray diffraction (XRD). The diffractograms were established with the CuKα radiation (λ=0.15405Å) on a Rigaku 0/20 diffractometer. Radiations are generated at near voltages of 50KV and a current of 30mA. XRD images were recorded in the range from 10 to 90° (in 2θ) with a step equal to 0.05° and a scan speed of 5°/min. The collected phases were sorted by comparison with references ICDD PDF-2-2014 (International Center for Diffraction Data – Powder Diffraction Files). The average crystallite size of the particles in powders was calculated using the Debye-Scherrer equation (Equation 1) from the respective XRD patterns [11]:

\[
\text{Crystallite size} = \frac{K \lambda}{\beta \cos \theta}
\]
\[ D_{hkl} = \frac{K \lambda}{\beta \cos \theta} \] (1)

Where: \( K \) is a constant function of crystallite shape, 0.8 < \( K \) < 1.1; \( K = 0.94 \) for FWHM of spherical crystals with cubic symmetry; \( \lambda \) is the wavelength of monochromatic radiation \( \lambda = 1.5405 \text{Å} \); \( \beta \) in radian is recognized as the Full Width at Half Maximum (FWHM) of the peak at the maximum intensity, \( \theta(hkl) \) is the peak diffraction angle that satisfies Bragg’s law for the (hkl) plane.

The degree of crystallinity (\( X_c \)) can be assessed as exposed in equation 2 [12]:

\[ X_c = \left( \frac{0.24}{\beta} \right)^3 \] (2)

**Micro Hardness Vickers Test**

A micro hardness test of the samples was carried out by a Vickers micro hardness tester (INNOVATEST, 4000 series, version 2.00). This test was achieved with 500g load applied for 10s using a diamond indenter. The indenter is formed of a square-based diamond pyramid with an angle of 136° at the top. The apparatus consists of a load range of 0.25; 0.5; 1; 2; 3; 5; at 10N exerted on an axis which has at its end Vickers point. The impression is analyzed using an optical microscope with two magnification lenses of 100 and 400 times. The automatic functional control gives a digital display. Vickers hardness is the quotient of a force applied to a surface and is calculated as follows:

\[ H_V = 1.854 \frac{P}{d^2} \] (3)

With \( H_V \) in (GPa), \( P \) (Kgf) the load that produces a diagonal imprint \( d \) (mm).

**Results and Discussions**

**XRD**

With chemical formula \( \text{Ca}_{10}(\text{PO}_4)_{6} (\text{OH})_2 \), the calcium phosphate hydroxyapatite (HA) derived from the crystallographic class apatites known \( \text{ME}_{10}(\text{XO}_4)_{6}(\text{Y})_2 \), isomorphic elements having the same hexagonal structure; where: \( \text{Me} \) regularly symbolizes a divalent cation, \( \text{XO}_4 \) a trivalent anionic group and \( \text{Y} \) an anion or a monovalent ionic group. Space group symmetry during crystallization of the hydroxyapatite is hexagonal \( P6_3/m \), more rarely monoclinic \( P2_1/b \) [13]. The matrix parameters of hexagonal hydroxyapatite are \( a = 9.432 \text{Å}, c = 6.881 \text{Å} \) and \( \beta = 120^\circ \), knowing that \( a = b \), et \( a = \beta = \gamma \). There also exists a stoichiometric and ordered form of hydroxyapatite crystallising in the monoclinic space group \( P2_1/b \) with \( a = 9.421 \text{Å}, b = 2a \) and \( c = 6.881 \text{Å}, \gamma = 120^\circ \). The monoclinic form of hydroxyapatite transforms to a hexagonal anion disordered form at 205°C. However, because this monoclinic form occurs only under special thermal conditions, crystal size is equal to 530.14 Å⁻¹. The stoichiometric hydroxyapatite is determined by a molar ratio \( \text{Ca}/\text{P} = 1.67 \) and a density of 3.156 [14].

The Figure 1 illustrates the X-ray diffraction patterns for hydroxyapatite samples according to the experimental procedure, i.e chemical synthesis explained previously. The entire XRD pattern shows diffraction lines characteristic of hydroxyapatite indexed in standards and in literature. The main phase as projected, is hydroxyapatite which is confirmed by superimposing results obtained with the ICDD – PDF 2 card: 01-072-1243. Figure 1 (a) shows the elaborate and uncalcined raw powder, where it is seen that the thermogram illustrates an amorphous structure. Figures 1 (b) and (c) show the thermograms of two powders heat treated at 900 and 1200°C. The fraction of amorphous phase decreases with increasing of the heat treatment temperature. As soon as the heat temperature was amplified, the hydroxyapatite peaks became sharper owing to a crystal expansion.
Assessment correlates to crystallites size for hydroxyapatite powders; in accordance with Debye-Scherrer’s formula (Equation 1) shows a relative enhance of crystallite size from 37nm to 49 nm with growing of the heat treatment temperature from 900 to 1200°C. Calculated crystallites size from hydroxyapatite thermograms correlates well with the crystallinity degree X_c computed using formula 2 presented in the previous section. The degree of crystallinity varies proportionally with the treatment temperature. When the temperature is 900°C we found X_c close to 54% and when the temperature reaches 1200°C we found an increase of X_c to a value of 72%; These results are also confirmed in literature [6].

**Mechanical Properties**

The micro indentation method was supported for the determination of compressive strength σ_r. The latter was calculated on the basis of the elastic limit. It has been shown that for brittle ceramics, the yield strength and the compressive strength are equivalent. Indeed, this material has no plastic domain. Therefore, it has been established that σ_e = σ_r. As regards ceramics among other materials, it has been shown that the yield strength σ_e is closely related to the hardness H_V according to the relation H_V = 3σ_e [15].

In our study, the Vickers microhardness method was used to measure hardness on heat treated hydroxyapatite pellets at 900°C and 1200°C. Often, heat treatment is used to improve the properties of a material. It results in consolidation, elimination of pores and densification of the grains within the material. The hardness taken from sintered or heat treated samples varies positively with the variation of the heating temperature, it increases from 1.97GPa when the temperature is equal to 900°C up to 3.23GPa when the temperature reaches 1200°C. In the work of F. Heidari et al., Hydroxyapatite was extracted from hen, goat and cattle bone. Samples were set by cold isostatic pressing method (CIP) and heat treatment at 1100, 1200 and 1300°C. The microhardness of the heated natural Hydroxyapatite increased with increasing the heat treatment and the maximum hardness was 3.7GPa at temperature of 1300°C. In fact, hardness increased with decreasing pores size [16]. In the study conducted by Ramesh et al., on

**FIGURE 1.** XRD thermograms of stoichiometric hydroxyapatite: (a) crude, (b) heated T 900°C, (c) heated T 1200°C
the Hydroxyapatite extracted from eggshells, the maximum Vickers hardness reached 5.62 GPa at sintering temperature of 1250°C [17].

In addition to the microhardness, other mechanical properties were measured namely the yield strength and the compressive strength. Indeed, in ceramic materials in compression these two properties are equivalent. We found that \( \sigma_e = \sigma_r \) varies as a function of the heating temperature. Its value is 65.8MPa when the temperature reaches 900°C, and it increases to a value of 111.076MPa when the temperature coincides with 1200°C. S. Laasri et al., conducted a study on the influence of sintering temperature on the breaking stress of hydroxyapatite and \( \beta\)-TCP. He observed that this mechanical characteristic increases with the sintering temperature to reach a maximum around 1160°C for \( \beta\)-TCP and around 1200°C for Hydroxyapatite. They are close to 45MPa for Hydroxyapatite and 50MPa for \( \beta\)-TCP [18].

The Vickers micro-indentation method also allows the calculation of toughness \( K_{IC} \) [19]. This mechanical quantity represented by the critical stress intensity factor \( K_{IC} \), expresses the resistance of a material to the sudden propagation of crack. If \( \sigma_c \) is the critical stress for which a length defect spreads sharply, according to the linear fracture mechanics \( K_{IC} \) is written as follows with \( \alpha = 1 \) in the case of an elliptical crack located at the center of a plate of infinite dimensions:

\[
K_{IC} = \alpha \sigma_c \sqrt{a} 
\]

The determination of the toughness from Equation 4 is conventionally done using standardized tests. These destructive tests require a large amount of material; also a lot of work is done to replace them with miniaturized and simpler tests, in particular the indentation test [20]. Indeed, the Vickers indentation method is simple to implement, it only requires a polished flat surface and an indentation device. The principle of this technique is to apply the indenter under a suitable load and then measures the length of cracks generated at the ends of the indenter impression. Toughness is calculated using the two parameters mentioned before, which are the load and the shape of the crack. In general, the Vickers indenter reveals four cracks at the ends of the cavity that propagate along the diagonal axis as shown in Figure 2 (a). On the other hand under the crack, several forms of cracks can appear. When the crack appears only at the ends of the impression, it is called Palmqvist type "P" (Figure 2 (b)), and when the indentation generates a crack in the form of a half Disk under the imprint it is said while it is of type Half Penny Crack or Median crack "M" (Figure 2 (c)) [21].

Several mathematical relationships exist for calculating toughness in ceramics. Nath et al.,[19] have used other models based on the elastic modulus \( E \). In this work we opted for the models of Shetty et al., [22] expressed in Equation (5) and that of K. Nihara [23] represented in Equation (6).

\[
K_{IC} = 0.0319 \frac{P}{(a e)^{0.5}} \]

FIGURE 1. Cracks obtained by Vickers indentation: (a) 4 cracks at the ends, (b) crack under the half penny crack or Median "type M" imprint, (c) crack under the Palmqvist imprint or "P type" [21].
These models are applied in "P-type" or Palmqvist cracks, which obey to the following criteria: c/a is small (c/a<3.5 or l/a<2.5) with c equal to (a + 1), (Figure 1). From these two models we have found that our Hydroxyapatite powder, produced by chemical synthesis and heated at temperatures between 900°C and 1200°C, has tenacities which vary with the heating temperature. For example at 900°C the toughness is 0.247MPa√m, and at 1200°C it reaches 1.047MPa√m. In general, hydroxyapatite is known by its weak mechanical properties especially its toughness $K_{IC}$ which is less than 1MPa√m, this material is much more used as a coating on medical prostheses because it cannot support the large loads exerted [24].

**Conclusion**

In this study, the mechanical and microstructural properties of the synthetic hydroxyapatite, with Ca/p stoichiometry equal to 1.67, were determined as a function of the temperature of the heat treatment. Three distinct cases are discussed. (1) unprocessed, crude hydroxyapatite. (2) heat-treated hydroxyapatite at a temperature of 900°C, and (3) at a temperature of 1200°C. The thermograms resulting from the XRD analysis reflect the influence of the variation of the temperature of the heat treatment on the structure of the material. It is clear that an amorphous structure developed within the material is transformed into a crystalline structure as the heat treatment temperature increases. Therefore, a clear improvement in the different mechanical properties is observed.

**REFERENCES**


