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Investigation of Microstructure and Mechanical Properties of Phosphocalcic Bone Substitute using the Chemical Wet Method

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Abstract. Selection of calcium phosphate base materials in reconstructive bone surgery is justified by the surprising similarities in chemical compositions with human bones. The closest to natural apatite material is the hydroxyapatite (HAp) which has a chemical composition based on calcium and phosphate ($Ca_{10}(PO_4)_6(OH)_2$). In this study, HAp is synthesized using the wet precipitation method from hydrated calcium chloride ($CaCl_2,12H_2O$) and di-sodium hydrogen phosphate di-hydrate ($HNa_2PO_4,2H_2O$). The powder is calcinated at 900°C and 1200°C in order to compare with sintered condition at 1150°C. Vickers microhardness tests and X-ray diffraction analyzes are used for the characterization of the crystalline material. Mechanical properties (H_V, σ_e, σ_r, *and* K_C) and the degree of crystallinity (X_c) are discussed according to heat treatment temperatures. Results indicate that heat treating the powder at 1200°C increased crystallinity up to 72%. At the same time, microhardness increased with temperature and even outmatched the sintered case at 1150°C. Fracture toughness is ameliorated with increasing heat treatment temperature by more than two folds.

INTRODUCTION

The aging phenomenon and the increased life expectancy of worldwide populations made the need for substitute materials and synthetic grafts which are proposed essentially to replace or repair and even regenerate lost natural bones. The main applications of hydroxyapatite (HAp,$Ca_{10}(PO_4)_6(OH)_2$) are in medical and dental fields. The precipitated powder is usually calcinated within the interval at 400-600°C or even at higher temperature to get a stoichiometric and apatitic structure [1].

(HAp) is a mixture based on calcium and phosphate and as a general rule it is used as bone graft to promote the growth of new bones [2]. Literature reviews show that phosphocalcic bone substitutes are increasingly looked-for in

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human therapeutics because of their microbiological safety and effectiveness [3]. One interesting property of calcium phosphate ceramics is the proportion between density and porosity which compares to bioactive materials.

Calcium phosphates contribute to the formation of the major mineral phase of human hard tissues. It is established that dissolution properties of calcium phosphates are strongly related to inherent physicochemical characteristics such as Ca/P molar ratio, crystallographic structure, pH and specific surface characteristics. In the various existing combinations of these calcium phosphates, the two ceramics that got the most attention are HAp, and TCP (tricalcium phosphate; $Ca_3(PO_4)_2$) as well as their mixtures [4].The structural, morphological and chemical properties of synthetic HAp can be controlled by changing the synthesis techniques and environments. Conventional procedures for HAp powder synthesis cover direct precipitation, hydrothermal techniques, hydrolysis of supplementary calcium phosphates, like solid state reactions and mechano-chemical approaches [5]. Wet precipitation is one of the most employed techniques which allow chemical reactions to take place between calcium and phosphorus ions below specific limits of pH and temperature.

The biological behavior of bioactive ceramic bone substitutes is quite well known. It appears that characterization should not be limited to biological properties alone but should be enlarged to assessment of the material resistance as a function of loads and usage time. Usually excessive fragility and fairly low mechanical properties of such materials are considered as disadvantages whenever they are exposed to higher applied stresses [6]. When considering complex relative motion of human beings, resistance and tribological properties, for instance, strength, elasticity, hardness, friction and roughness which have important roles at interfaces between prosthetic parts and the basic bone added to the contact with the different body physiological fluids.

The objective of this study is to investigate crystallinity and toughness characteristics of hydroxyapatite powder produced by wet precipitation method. In addition, the effect of calcination temperature chosen around the usual sintering conditions of HAp is discussed.

Experimental Work

Preparation of the Hydroxyapatite Powder

The aqueous precipitation synthesis method also known as the chemical wet method is used to synthesize HAp from both hydrated calcium chloride ($CaCl_2$,$12H_2O$) as a source of calcium and dehydrated di-sodium hydrogen phosphate (HNa_2 PO_4, $2H_2O$) as a source of phosphate. The prescribed molar stoichiometry ratio of Ca:P for the product is 10:6 and a pH of 9 is imposed. Reaction conditions are set for a temperature of 80°C, a stirring speed of 300 rpm, a flow rate of 5ml/min and finally a duration time of 60 min. The synthesized powder is subsequently put into the form of pressed pellets of diameter of 10mm and thickness <3.5 mm. Then, the hydroxyapatite pellets are heated treated at 900°C and at 1200°C. The procedure involved a temperature increase at a rate of 10°C/min and a calcination period of 90 min while the sintering condition (1150°C) is performed at 5°C/min and a holding time of 180 min.

X-Ray Diffraction

The identification of the crystalline phases present in the elaborated powders is carried out by X-ray diffraction (XRD) and the diffractograms are established using CuKα radiation (λ=0.15405Å) on a Rigaku θ/2θ diffractometer. Radiations are generated at 50 kV and 30mA. XRD images are recorded in the range [10°-90°] (2θ) with a step of 0.05° and a scan speed of 5°/min. The collected phases are 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 are calculated using the Debye-Scherrer equation from the respective XRD patterns [7]:

$$D_{hkl} = \frac{K\lambda}{\beta_0 \cos\theta} \tag{1}$$

where: Kis taken as 0.94 for Full Width atHalf Maximum (FWHM) of spherical crystals with cubic symmetry; λ is the wavelength of monochromatic radiation (1.5405Å),$\beta_0$is recognized as the FWHM peak atthe maximum intensity, θ(hkl) is the peak diffraction angle that satisfies Bragg's law for the (hkl) plane. Subsequently, the degree of crystallinity (X_c) can be calculated using equation 2 [8]:

$$X_C = \left(\frac{0.24}{\beta_0} \right)^3 \tag{2}$$

Microhardness Vickers Tests

Microhardness measurements are carried out by a Vickers microhardness tester (INNOVATEST, 4000 series, version 2.00). A load of 500g is applied for 10s on a diamond indenter to obtain an imprint. The indentation is performed via a square-based diamond pyramid with an angle of 136° at the top. The impression is analyzed using an optical microscope at two magnification levels (100X and 400X). The automatic functional control allows reading the measurements from a digital display. Vickers hardness is the quotient of an applied force (P) to a surface represented by the square of the imprint diagonal (d^2)and is calculated as follows:

$$H_V = 1.854 \frac{P}{d^2} \tag{3}$$

where H_v is in (GPa), P is in (Kgf) and d in (mm).

Results and Discussion

Microstructure

The calcium phosphate hydroxyapatite (HAp) is derived from the crystallographic class of apatites known as $ME_{10}(XO_4)_6(Y)_2$. These are isomorphic elements having the same hexagonal structure. In this case, ME regularly symbolizes a divalent cation, XO_4 a trivalent anionic group and Y an anion or a monovalent ionic group. Space group symmetry during crystallization of the hydroxyapatite is hexagonal $P6_3/m$, more rarely monoclinic $P2_1/b$ [9]. The chemical formula of the pure HAp used in this study is $Ca_{10}(PO_4)_6$ $(OH)_2$. The matrix parameters of hexagonal hydroxyapatite are a=9.432Å, c=6.881 Å and β=120° and for this case, it is noted that a=b, and α=β=γ. There also exists a stoichiometric and ordered form of hydroxyapatite crystalline in the monoclinic space group $P2_1/b$ with a=9.421A°, b=2a and c= 6.881A°, γ=120°. However, at 205°C, the monoclinic form of hydroxyapatite may transforms to a disordered hexagonal anion since it can occur only under such special thermal conditions and crystalsize is equal to 530.14 $Å^3$.

Figure 1 illustrates the X-ray diffraction patterns for hydroxyapatite samples obtained according to the experimental procedure. Figure 1a shows the amorphous structure of the uncalcined raw powder. The main phase as projected is hydroxyapatite which is confirmed by superimposing results obtained with the *ICDD – PDF 2 card: 01-072-1243*. Figures 1b) and 1c show the thermograms of the two powders heat treated at 900°C and 1200°C. The fraction of amorphous phase decreases with increasing of the heat treatment temperatureand the hydroxyapatite peaks became sharper owing to a crystal expansion.

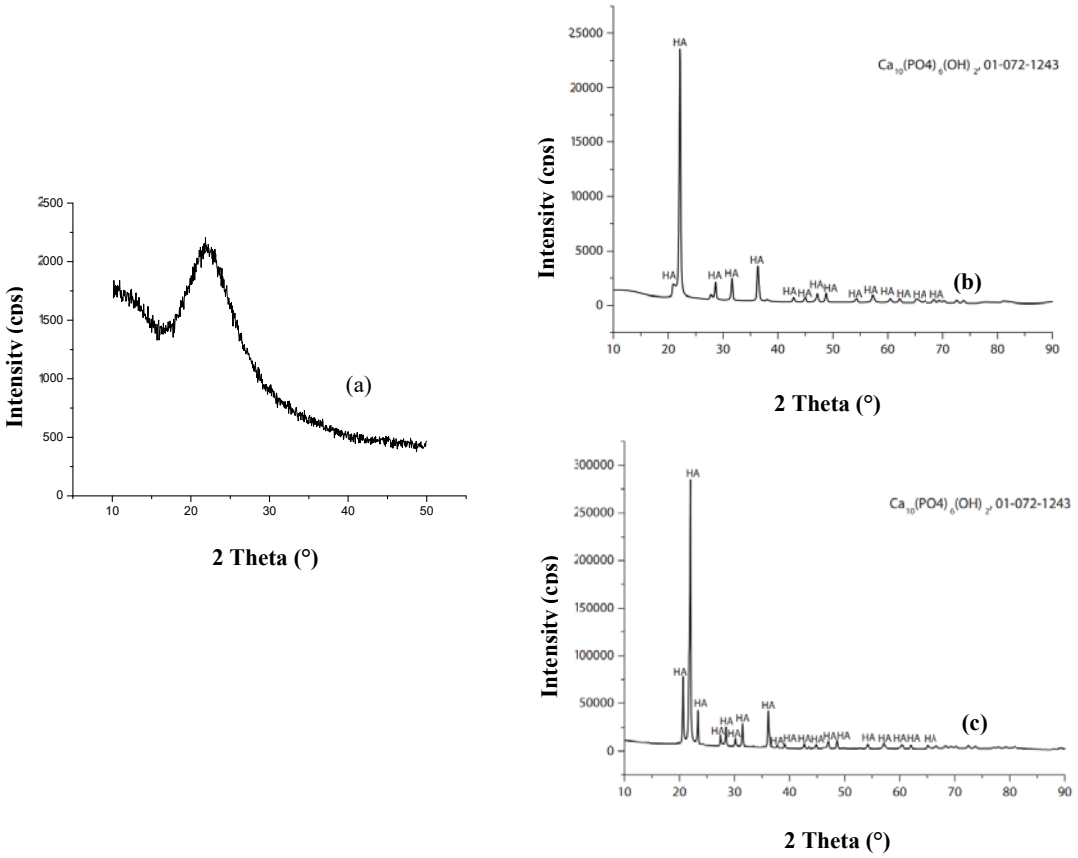

FIGURE 1. X-ray diffraction thermograms of stoichiometric HAp:
(a) Crude; (b) and (c) Heat treated cases at 900°C and 1200°C respectively.

Correlation of crystallitesize for hydroxyapatite powders in accordance with Debye-Scherrer's formula (Equation 1) shows a relative enhancement of crystallite size from 37nm to 49 nm when heat treatment temperature evolves from 900°C to 1200°C. Calculated crystallites size from Hap thermograms correlate well with the crystallinity degree X_c computed using (Equation 2). The degree of crystallinity varies proportionally with the treatment temperature. When the temperature is 900°C, X_c is close to 54% whereas at 1200°C, it jumped to 72%.This could be explained by the rearrangement of the structure which becomes more consolidated and suggesting better eventually mechanical properties.

Mechanical Properties

The Vickers micro-indentation method allows the calculation of fracture toughness from imprint edge cracks [10,11]. It is known that the critical stress intensity factor (K_C) represents the resistance of a material to the sudden crack propagation. Based on linear fracture mechanics for the case of an elliptical crack located at the center of a plate of infinite dimensions and considering σ_c as the critical stress for which a crack initiates, K_C is written as follows :

$$K_C = \alpha \sigma_C \sqrt{\pi a} \tag{4}$$

where a (in mm) is the crack length and α is a shape factor close to unity.

The determination of the toughness from Equation 4 is conventionally done using standardized tests which require a large amount of material. Also, a lot of research work has been done to validate miniaturized and simpler tests, in particular the indentation test [12]. In general, the Vickers indenter reveals four cracks at the ends of the cavity that propagate along the diagonal axis as shown in Figure 2a. When the crack appears only at the ends of the impression, it is called Palmqvist type "P" (Figure 2b). On the other hand, when the indentation generates a crack in the form of a half-disk under the imprint, it is said Half Penny Crack or Median crack "M" (Figure 2c) [13].

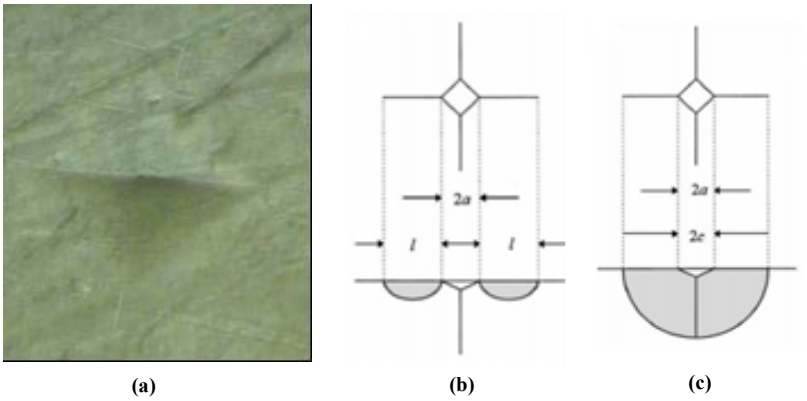

FIGURE 2. Cracks obtained by Vickers indentation: (a) Four cracks at the ends, (b) crack under the Palmqvist imprint or "P type", (c) Half penny crack or “M type” imprint [13].

Several mathematical relationships exist for calculating toughness in ceramics [11,14,15]. Respectively based on references [11] and [15], Kc can be expressed in the following forms:

$$K_C = 0.0319 \frac{P}{(a.c)^{0.5}} \tag{5}$$

$$K_C = 0.203\left(\frac{c}{a}\right)^{-1.5} H_V (a)^{0.5} \tag{6}$$

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 + l), (Figure 2b).

The microindentation data are used to compute compressive strength (σ_r) which is equivalent to the elastic limit (σ_e) for brittle materials. Indeed, the HAp material does not show any plastic domain at all during compression tests. For brittle materials such as ceramics, it has been shown that the yield strength (σ_e) is closely related to the hardness (H_V)in accordance to the following relationship [16]:

$$H_V = 3\sigma_e \tag{7}$$

Usually, sintering at high temperatures is recommended for mechanical properties improvement. In this study a simple calcination operation is investigated for the same purpose as sintered condition. It is observed that hardnessvaried positively with the increase of heating temperature i.e., it increased from 1.97GPaat 900°C up to

3.23GPaat 1200°C (Figure3a). HAp can be extracted from natural sources such as hen, goat and cattle bone by cold isostatic pressing method (CIP) [17]. For samples sintered at 1100°C, 1200°C and 1300°C, it is shown that microhardness increased with temperature reaching 3.7 GPa. This is accompanied with pores size decreasing. For HAp extracted from eggshells and sintered at 1250°C, Vickers hardness reached a maximum of 5.62 GPa [18]. The influence of sintering temperature on the breaking stress shows that mechanical characteristic are enhanced to maximum levels at 1160°C and 1200°C respectively for β-TCP and HAp. Observed compressive strengths at these conditions are whining the range 45 to 50 MPa for both HAp and β-TCP [10]. In addition to microhardness, other mechanical properties are studied namely the yield and the compressive strengths. It is found that σ_r is 67 MPa at 900°C and it increased to 108 MPa at 1200°C (Figure3b).

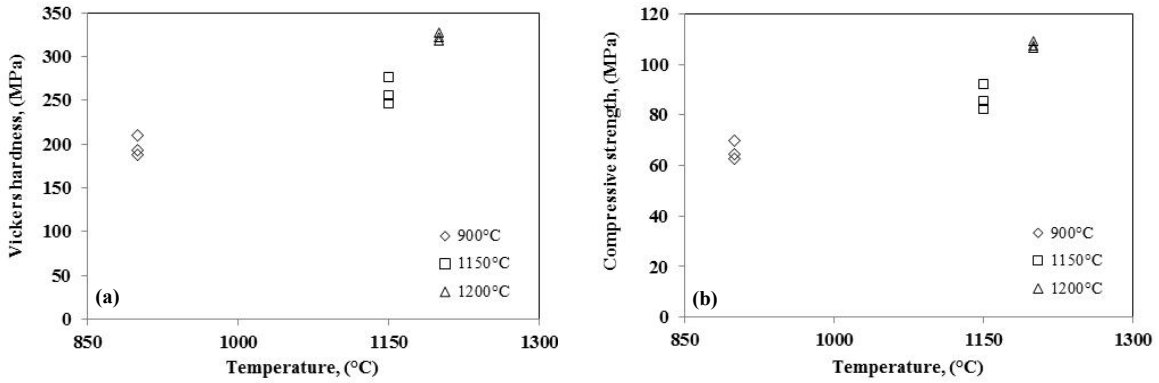

FIGURE 3.Mechanical properties using Vickers microhardness for synthesized HAp by calcinations at 900°C and 1200°C and compared to sintered at 1150°C; (a) Hardness, (b) Compressive strength.

Equations (5) and (6) have been used to calculate fracture toughness for HAp. It is found that at 900°C; K_c is 0.247MPa√m and at 1200°C it grew to 0.70 MPa√m. Figure 4 shows these results together with sintered value of K_c at 1150°C. It is observed that the latter is lower than that of 1200°C. Equation (5) seems to overestimate K_c values and those given in literature are closer to results using equation 6.

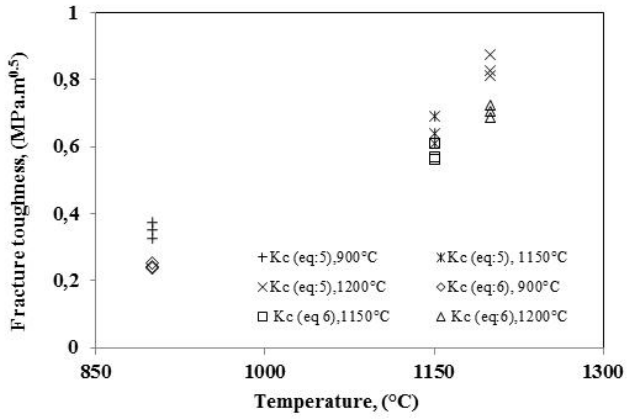

FIGURE 4. Fracture toughness for synthesized HAp by calcinations at 900°C and 1200°C and compared to sintered at 1150°C.

In general, HAp is recognized by its weak mechanical properties especially its toughness K_c which is less than 1MPa√m [11,14,15]. Table 1 summarizes literature data for mechanical properties for various Ca–P-based materials

with different processing conditions and compares them to those obtained in this study. It is observed the process temperature interval is usually between 900°C and 1450°C. The synthesized HAp shows lower values of H_v but interesting strength limits going up to 108 MPa. For K_c pure HAp value are close especially for the 1200°C case while the 900°C was 58% lower. The elastic modulus was deduced from K_c values and it was 20% lesser [14].

TABLE 1.Comparison of mechanical properties for various Ca–P-based materials with different processing conditions.

Material	**Processing Conditions**	**Vickers Hardness (GPa)**	**Compressive Strength (MPa)**	**Fracture Toughness* ($MPa.m^{0.5}$), (Eq. 6)**	**Elastic Modulus (GPa)**	**REF.**
Pure HAp sintered for 2h	Synthesis, suspension-precipitation, (CaO,H_3PO_4), 1200°C	6.1	54	0.6	117	[14]
HAp, Gel casting	Sintered at 1250°C	4.45		0.95	138	[19]
HAp - Al_2O_3-CaF_2	Pressing, sintering at 1450°C	7		1.15	140	[20]
HAp-ZrO_2 (20-60 wt %)	Chemical co-precipitation, 4h, 1250°C	0.15-0.35**	51-115	-	-	[21]
Porous Ceramic ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$); sintered	900°C	0.57		0.57	33.4	[22]
	1000°C	0.81		0.68	52.7	
	1100°C	2.26		0.74	86.8	
	1200°C	6.12		1.13	178	
β-TCP chemical wet method $(NH_4)_2HPO_4$ and $Ca(NO_3)_2$ $4H_2O$; sintered 3h	1100°C	7.4		1.2	94.8	[10]
	1160°C	9		1.4	96.2	
	1200°C	8.7		1.35	93.8	
	1250°C	5.1		0.88	89	
Synthesized HAp, (Wet Method)	Treated at 900°C	0.197	67	0.25	76	*This Study*
	Treated at 1200°C	0.323	108	0.70	96.4	
	Sintered at 1150°C	0.260	89	0.58	92.4	

* *Calculated (when needed) using Eq. 6.*
***Calculated (when needed) from compressive strength using Eq. 7.*

Conclusion

In this study, microstructural and the mechanical properties of synthetic HAp were studied using X-ray diffraction and microindentation. It was found that heat treatment at 1200°C increased crystallinity up to 72%. Also, microhardness increased with temperature and outmatched the sintered case at 1150°C. Similarly, fracture toughness is ameliorated with heat treatment temperature by more than two folds. It is concluded that heattreatment in the form of a calcination (at the same level of sintering temperatures) improved HAp mechanical properties and contributed to the consolidation of the material by pores elimination anddensification of the grains.

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