

Elaboration and Characterization of Bioceramics from Natural Phosphate

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The aim of this work is the substitution of the bovine bone by the natural phosphate from Djebel-Onk (Tébessa, East of Algeria). We prepared two composites (bone/ Al_2O_3 and natural phosphate/ Al_2O_3) by reaction sintering. Different experimental techniques, including density, porosity, X-rays diffraction, and SEM techniques, were used to analyze the formation and transformation of phases at different temperatures. From the X-ray diffraction patterns, we put in evidence the formation of several phases. Through these results, we lighted the possibility of preparing bioceramics from natural phosphate (bone and natural phosphate). The presence of the different materials was confirmed by the micrographic observations.

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1. Introduction

Hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) and β -tricalcium phosphate (β -TCP, $\text{Ca}_3(\text{PO}_4)_2$) materials are very popular restorations since they accelerate the bone growth around the implant, because are very similar to the mineral part bone and are highly bioactive and biocompatible [1, 2]. However, the principal limitation of these materials is that has low fracture strength, low toughness and poor fatigue resistance, which restricts the clinical orthopedic and dental applications [3, 4]. The incorporation of a ceramic second phase dispersed in a ceramic matrix is known to improve the mechanical properties [5, 6]. HA and β -TCP materials must be reinforced by alumina, because it is also classified as a bioinert material. In addition, alumina has been used in orthopedic applications due to its excellent wear resistance and high hardness [7]. However, when this oxide is used as a reinforcing agent for HA, the decomposition of HA to β -TCP occurs strictly. Many methods for synthesizing HA have been reported, such as sol-gel process [8], wet synthesis [9], and the hydrothermal method [1]. The HA prepared from the bovine bone is advantageous, because it is environment-friendly [8]. The purpose of the present investigation is to synthesize bioceramic composites from bovine bone and natural phosphate. The phase evaluation, thermal analysis, and microstructure observations were carried out for the produced samples.

2. Material and equipment

Bovine femoral bone, natural phosphate, and alumina (Al_2O_3) were used as the raw materials. The bovine bone were cut into small pieces and washed in an alkali solution. The bone pieces were calcinated at 850°C for 2 h

in air and then crushed and ball milled until fine powders. The natural phosphate was extracted from the mine of Djebel-Onk (East of Algeria), their crystallographic analysis and chemical compositions are given in previous work [11]. The natural phosphate was calcinated at 900°C in air to totally release the organic material. The alumina content in the laboratory aluminum oxide provided by Sigma Aldrich was 98%. Two compositions were prepared by the mixture of 50 wt% of bovine bone and 50 wt% of Al_2O_3 (bone/ Al_2O_3), and the mixture of 50 wt% of natural phosphate and 50 wt% of Al_2O_3 (natural phosphate/ Al_2O_3).

The raw materials are mixed and ground to homogenize the compositions and increase the reactivity of the powders. The ball-milling experiments were performed through planetary ball mill (Pulverisette 6) for 5 h. The slurry was dried at 110°C , powdered and sieved through a $100\ \mu\text{m}$ mesh, then compacted at a pressure of 100 MPa using a cold uniaxial press. In order to determine an optimum preliminary sintering temperature, the compacts were sintered under atmospheric conditions at different temperatures within the range 1100 – 1600°C with a step of 50 K for 2 h of soaking and cooled down inside the furnace. The heating rate was kept constant and equal to $10^\circ\text{C}/\text{min}$.

The X-ray diffraction (XRD) analyses were carried out using a Bruker D8 diffractometer. The XRD tests conditions were Ni-filtered Cu K_α X radiation (35 kV–30 mA) with a scanning speed of 37° (2θ) per minute and at an increment of 0.02° . The apparent density and open porosity of fired samples were determined by the Archimedes method using distilled water. The micrograph of the samples was observed by scanning electron microscopy (SEM) (JEOL JSM-7001F).

3. Results and discussion

XRD patterns obtained from the samples heated at different temperatures are shown in Fig. 1. The XRD spectra for natural phosphate/ Al_2O_3 samples show the

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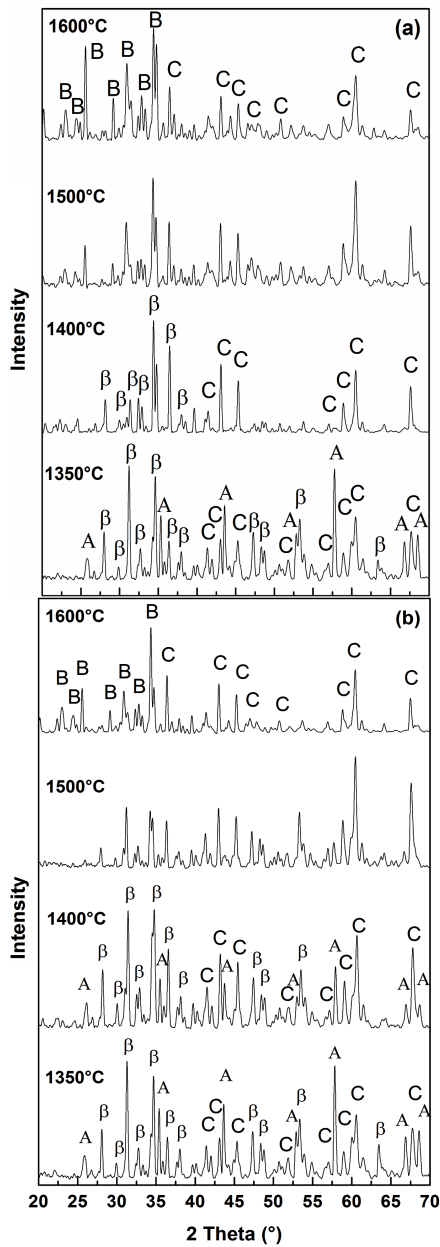
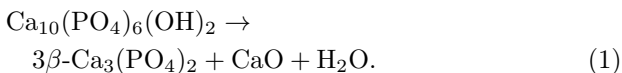


Fig. 1. XRD patterns of the mixture of (a) natural phosphate/ Al_2O_3 and (b) bone / Al_2O_3 at different heat treatment temperature. A: alumina, β : β -TCP, C: CA_6 , B: CA_2 .

presence of three phases of alumina, β -TCP and hibonite (CA_6 , $\text{CaO}(\text{Al}_2\text{O}_3)_6$) at 1350°C (Fig. 1a). It is well known that at high temperatures, pure HA dissociates and forms β -TCP, H_2O and CaO [12]. This last reacts with alumina to yield CA_6 [8]. The possible reaction associated with the dissociation of pure HA can be expressed as [12]:



At 1400°C the peaks corresponding alumina phases disappeared and the intensity of β -TCP decreases. This is

due to the complete reaction between alumina and CaO and the dissolution of β -TCP in CaO and P_2O_5 . As the sintering temperature increased to 1500°C , the intensity of CA_6 is gradually increased, when the intensity of the peaks corresponding to β -TCP disappeared. Also, we note the presence of new phase of CA_2 ($\text{CaO}(\text{Al}_2\text{O}_3)_2$). At 1600°C , the intensity of the peaks corresponding to CA_2 is notably increased. Simultaneously with these increases, the CA_6 intensity decreases.

In the samples bone/ Al_2O_3 (Fig. 1b), there is any modification of the formed phases at 1350°C compared with precedent sample. We note the presence of three phases of alumina, β -TCP and CA_6 . The intensity of the peaks corresponding to alumina and β -TCP is notably decrease with temperature (1400 – 1500°C). Simultaneously with these decreases, the CA_6 intensity increases. The presence of alumina at 1400°C confirms that the reactivity of alumina with CaO is lower than natural phosphate/ Al_2O_3 samples. At 1600°C , new phases of CA_2 were detected in these samples. The presence of impurities in natural phosphate is responsible for the total reaction between CaO and alumina and the formation of CA_2 at a lower temperature.

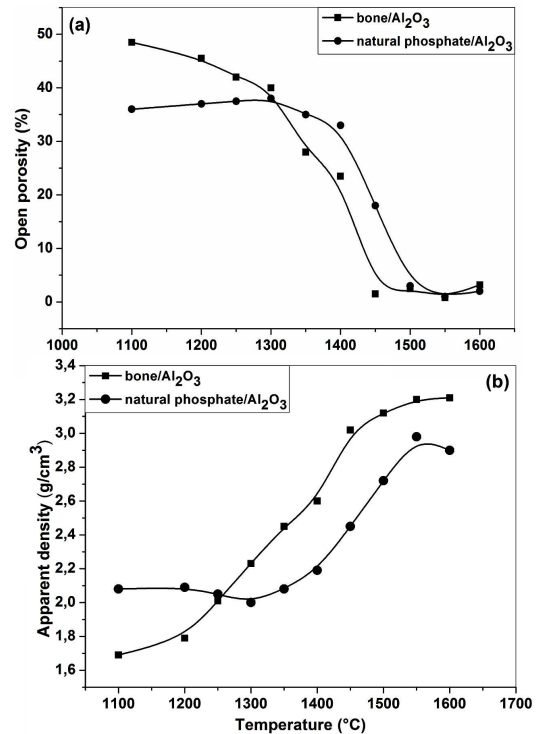


Fig. 2. Open porosity (a) and apparent density (b) of samples as a function of sintering temperature.

Figure 2 shows the variation of open porosity and apparent density as a function of the sintering temperature. Between 1100 and 1300°C the open porosity values are practically constant in the case of natural phosphate/ Al_2O_3 samples (Fig. 2a). At high temperature (1300 and 1500°C) a large decrease of open porosity is observed which may be due to the completely closed

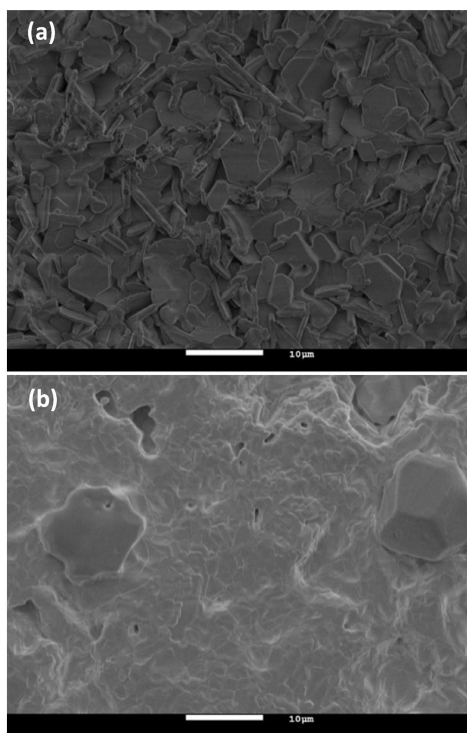


Fig. 3. Microstructures of the composites sintered at 1600 °C for 2 h of (a) bone/Al₂O₃ and (b) natural phosphate/Al₂O₃.

of pores. Between 1500 and 1600 °C the open porosity reached small values (2%). Gradual decrease in the open porosity was observed for the bone/Al₂O₃ sample from 1100 to 1300 °C. After 1300 °C there is a dramatical decrease of open porosity and reaches small values (1.5%) at 1450 °C. At high temperature the open porosity is practically constant in the both cases.

The density is a very interesting parameter used to characterize sintered samples. Figure 2b shows the densification behavior (apparent density) of the samples as a function of the sintering temperature. The apparent density of the natural phosphate/Al₂O₃ samples showed the same values from 1100 to 1300 °C. After 1300 °C, we note that the apparent density increases linearly and reaches the maximum value at 1550 °C (2.98 g/cm³), then decrease to 2.9 g/cm³ at 1600 °C. In the case of bone/Al₂O₃ samples, the apparent density was practically constant between 1100 and 1200 °C. The values of the apparent density of this sample are lower than for natural phosphate/Al₂O₃ samples. After 1200 °C, we note a gradual increase in the apparent density up to 1450 °C. Between 1500 and 1600 °C we note a slight increase in the apparent density to maximize at 3.21 g/cm³. In general, the change of the apparent density is back to some factors such as: crystalline phases, glassy phases, porosity and sintering aids.

Figure 3 shows the microstructure of composites sintered at 1600 °C for 2 h. The grains of bone/Al₂O₃ appear with globular form and hexagonal plate. The hexagonal grain confirms the formation of CA₆ (Fig. 3a). For the samples prepared from natural phosphate/Al₂O₃ (Fig. 3a), we note the presence of irregular grain with a non-crystalline phase and homogeneous microstructure.

4. Conclusion

The synthesis of bioceramics from natural phosphate has been shown to be possible by bone and natural phosphate. In this work, two composites (bone/Al₂O₃ and natural phosphate/Al₂O₃) were prepared. The addition of alumina to bone and natural phosphate leads to:

- The decomposition of HA into β -TCP and CaO at 1350 °C and the formation of new phases such as: hibonite CA₆ and β -TCP at low temperature and CA₆ and CA₂ at high temperature.

- The increase of apparent density sharply of the samples with increase of temperature and the decrease of the open porosity of two composites due to the formation of a glassy phase during the sintering process.

- The possibility of preparing bioceramics from natural phosphate (bone and natural phosphate).

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