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Physical Properties of Calcium Phosphate-Alumina Bio ceramics as Dental Implants

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Abstract

In order to perform new dental implant, we carried out investigations on α -alumina and calcium phosphate based composites. α -Alumina nano-powder were synthesized using reverse micelle method while calcium phosphate nano-powders with different molar ratio starting from 1.8 to 1.1 were synthesized by precipitation method, using calcium nitrate (Ca(NO₃)₂·4H₂O) and ammonium hydrogen orthophosphate (NH₄H₂PO₄) as precursor materials as source for calcium (Ca²⁺) and phosphate ((PO4)³⁻) ions respectively. Samples of respectively 5, 10 and 20% weight of Calcium phosphate powder were mixed with alumina, consolidated and sintered at 1400°C for 4 hours. The synthesized composites, in form of pellets were characterized for bulk density, apparent porosity, hardness and flexural strength properties.

Keywords: Bio ceramics; Bulk density; Porosity; Hardness; Flexural strength

Introduction

Bioceramic materials particularly calcium phosphate based materials are used mainly as bone substitute or scaffolds due to their good biocompatibility, and their compositional similarity with the inorganic components of human bone [1]. Many of these bioceramic materials also possess excellent chemical resistance, compressive strength and wear resistance. However, there are some bioceramic materials which are inert in their bioactive response. This implies that the "bio inert" biomaterials lacks strong bond at the interface between the implant and the host tissue and are bonded through a fibrous capsule of non-adhering tissue [2]. Calcium phosphate based ceramics has a wide range of composition where phases are either bio-active or bio-resorb able and hence finds wide range application in repairing musculoskeletal disorder as well as bone augmentation in defect or diseased side of human body [3]. Hence, Calcium phosphates (Cap) have been sought as biomaterials for reconstruction of bone defect in maxillofacial, dental and orthopaedic applications [4]. However, calcium phosphate-based materials have attracted considerable interest in orthopaedic and dental applications because of their biocompatibility and tight bonding to bone, resulting in the growth of healthy tissue directly onto their surface [5]. Among them, Apatite has been investigated as an alternative biomedical material. Apatite has also been considered as an attractive material for its similarity in structure and composition to bone. In vitro studies have shown that apatite is biocompatible, has a better stability and ensures the formation of a mechanically and functionally strong bone [6]. Consequently, calcium phosphate compounds have been used as bone graft substitutes in many surgical fields such as orthopaedic and dental surgeries [7]. This use leads to an ultimate physicochemical bond between the implants and bone- termed osteointegration. Even so, the major limitation to the use of some calcium phosphate based ceramics as load-bearing biomaterial is their mechanical properties which make it brittle, with poor fatigue resistance (9,10,14 and 19-22). Moreover, the mechanical properties of calcium phosphate are generally inadequate for many load-carrying applications (10, 14, 19, 20, 21, 22, 23). Its poor mechanical behaviour is even more evident when used to make highly porous ceramics and scaffolds. Hence, metal oxides ceramics, such as alumina (Al₂O₂), titania (TiO₂) and some oxides (e.g. ZrO₂, SiO₂) have been widely studied due to their bioinertness, excellent tribological properties, high wear resistance, fracture toughness and strength as well as relatively low friction [8]. However, bio inert ceramic oxides having high strength are used to enhance the densification and the mechanical properties of ceramics based on calcium phosphate. In this paper, we will try to improve the physical properties of calcium phosphate by introducing a bio inert oxide like alumina. Indeed, Alumina $(\alpha$ -Al₂O₃) was the first bioceramic widely used clinically. It is used in load-bearing hip prostheses and dental implants because of its combination of excellent corrosion resistance, good biocompatibility, and high wear resistance and high strength. Alumina is reported to be bio-inert until its grain size is in nano scale [9]. The aim of this work was to elaborate a Calcium phosphate - a -Alumina composites as a dense material having adequate mechanical properties to be used essentially as dental implants and to study their mechanical properties. Hence this work focuses on preparing biphasic Calcium phosphate - a -Alumina composites, to investigate on the sintering behaviour and to characterize the physical and in particular mechanical properties of the nano composite.

Materials and Methods

Synthesis of samples

Calcium phosphate powder: Calcium phosphate samples required in the study were prepared by precipitation method (5-8). Six different batches of calcium phosphate with varying Ca/P molar ratio (1.8, 1.67, 1.5, 1.33, 1.21 and 1.1) were synthesized [10]. Calcium nitrate (Ca(NO₃)₂.4H₂O) and ammonium hydrogen orthophosphate (NH₄H₂PO₄) were taken as precursor materials as source for calcium (Ca³⁺) and phosphate ((PO₄)³⁻) ions respectively. Ammonia solution was taken as the precipitant (Table 1) [11]. Resume the amount of

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Received December 04, 2014; Accepted February 23, 2015; Published March 22, 2015

Citation: Hafid M, Belafaquir M, Merzouk N, Al Gana H, Fajri L (2015) Physical Properties of Calcium Phosphate-Alumina Bio ceramics as Dental Implants. Bioceram Dev Appl 5: 083. doi:10.4172/2090-5025.1000083

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Ca/P Molar Ratio	Weight ratio of (Ca(NO ₃)2.4H ₂ O/NH ₄ H ₂ PO ₄) taken for synthesis
1.8	12.744 : 3.45
1.67	11.823 : 3.45
1.5	10.62 : 3.45
1.33	9.416 : 3.45
1.2	8.496 : 3.45
1.1	7.788 : 3.45

 Table 1: Amount of precursors taken for synthesis of calcium phosphate nano powder with different Ca/P molar ratio.

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The amount of precursor materials taken are mixed properly and a solution is made [12]. The PH of the solution is maintained at 10 by adding ammonia solution. The solution is stirred for 5-6 hours and after that it is allowed to precipitate[13]. Then the precipitate is washed thoroughly by distilled water by centrifugal process in the Centrifuge apparatus (Centrifuge cycle: 8000 rpm for 5 minutes). Each sample is washed properly for 3 times. Then finally each sample is dried in Vacuum drier at 80°C for 24 hours.

a-Alumina powder: Alumina powders were synthesized via Reverse Micelle process (9), 200 g of Aluminium nitrate $(Al(NO_3)_3.9H_2O)$ was taken in 400 ml water. A quantity of 2000 ml Cyclohexane was added to the aluminium nitrate solution and properly stirred [14]. Now surfactant, Triton-X was added drop wise with continued stirring until a translucent or milky solution is formed. Then equal amount of co-surfactant, Butanol was added [15]. Now the pH of the solution is maintained at 10 by adding precipitant, ammonia solution. The solution is properly stirred and allowed to precipitate. The precipitate was washed with Propan-2-ol and filtered with Whatman-40 filter paper.

Al $(NO_3)_3.9H_2O + NH_4OH \rightarrow Al (OH)_3 + NH_4NO_3$

The filtrate is then dried in Vacuum oven at 80°C and the dried powder is calcined at 1200°C to form alumina powder (Al,O₃).

Calcium phosphate–Alumina composites: Amount of 5, 10 and 20 weight % of Calcium phosphate powder (6 batches) was mixed with alumina powder separately to form composites with different composition [16]. Each batch of composite was added with 3% PVA binder and pressed to form 0.5 g of pellets in a 12 mm cylindrical die. The green pellets are pressed at 4 Tonn pressure and given a dwell time of 90 seconds. The green pellets were then sintered at 1400°C with a soaking time of 4 hours [17]. The firing cycle was composed of 500°C with soaking time 2 hours, for binder burn out and 1400°C with 4 hours of soaking time, for sintering.

Characterisation

X-Ray Diffraction (XRD) and SEM

The XRD of synthesized samples were obtained using a Philips X-Ray diffractometric (PW 1730, Holland) with a Cu-Ka radiation and Ni filter (λ =1.5406 Å) at 40 kV and 30 mA having a scan range (2° θ) of 10-60° for calcium phosphate powder and 10-80° for alumina powder, at a scan speed of 0.04 (2° θ /sec) [18]. While morphology studies were performed using a scanning electron microscopy (SEM–JSM 360LV).

Bulk density (BD) and Apparent porosity (AP)

Density and porosity (BD and AP) were measured using the

Archimedes buoyancy technique with dry weights, soaked weights and immersed weight in water [19]. The sintered pellets of the samples were immersed in 3 hours boiled water until no vapours were seen coming out from the pellets. Afterwards, the dry, soaked and suspended weight of the pellets was calculated.

Bulk Density and apparent porosity were calculated following the respective formula:

$$Bulk Density = \frac{Soaked Weight}{Soaked Weight - Suspended Weight} \times Density of liquid$$

Apparent Porosity = $\frac{\text{Soaked Weight} - \text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}} \times 100\%$

Vickers hardness (HV)

The sintered pellets of the composites were polished properly with Emery paper and the hardness of the pellets was carried out by Vickers Hardness Tester [20].

The Vickers hardness test uses a square-based pyramid diamond indenter with an angle of 136° between the opposite faces at the vertex, which is pressed into the surface of the test piece using a prescribed force, F. The time for the initial application of the force is 2 s to 8 s, and the test force is maintained for 10 s to 15 s. After the force has been removed, the diagonal lengths of the indentation are measured and the arithmetic mean, d, is calculated. The Vickers hardness number, HV, is given by:

HV=Constant×Test force/Surface area of indentation

$$= 0.102 \times 2F\left(\sin\frac{136^\circ}{2}\right)/d^2$$

Bi-axial flexural strength

Rectangular test pieces with dimensions 50 mm×70 mm, and square test pieces with dimensions 50 mm×50 mm of the studied ceramics were used in this study. Average thickness of the both the rectangular and square test piece was about 0.42 mm. In this study, the load was applied to the specimen center with a flat punch of radius 1.8 mm. Specimens were simply supported by bearing balls of 1.95 mm radius to eliminate the friction between the support balls and the specimen. The location of the bearing balls, which lay in dimples on a steel base plate, was different for the rectangular and square test piece measurements. Dimples with radius 2 mm and 5 mm apart were machined on the steel base plate of dimensions 17 mm×100 mm×100 mm. Strength measurements were done with a 100 N Instron 8562 Universal Testing Machine using a 100 N load cell.

Results and Discussion

An X-ray diffraction pattern, typical of the composites, is shown in Figure 1. Hydroxyapatite (JCPDS 34-0010), as a predominant phase in the sample, can be identified from this reflection pattern [21].

In other hand (Figures 2a-2c). Shows a typical SEM pictures of sintered composite, for instance 5% CaP (1.8) 95% Al_2O_3 , 5% CaP (1.67) 95% Al_2O_3 , and 10% CaP (1.67) 90% Al_2O_3 , respectively.

The obtained SEM images show that the average grain size of the sintered calcium phosphate alumina composites is about 1 μ m while





Figure 2a: SEM image of 5% CaP (1.8) 95% Al₂O₃ sintered composite.



Figure 2b: SEM image of 5% CaP (1.67) 95% Al₂O₃ sintered composite.



Figure 2c: SEM image of 10% CaP (1.67) 90% Al₂O₃ sintered composite.

the microstructure shows an open porosity in samples.

Bulk density and apparent porosity results

Figure 3 shows the bulk density distribution of the sintered calcium phosphate–alumina composite. The sample nos. 1, 2, 3, 4, 5 and 6 correspond to the weight % of CaP nano powder with different Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1 respectively mixed with 95, 90 and 80% weight alumina.

Composition with Ca:P molar ratio of 1.67 and 5% weight of CaP shows the highest bulk density of 3.76 g/cc, while the composition with Ca:P molar ratio of 1.2 and 10% weight of CaP shows the highest bulk density of 3.43 g/cc and those with Ca:P molar ratio of 1.67 and 20% weight of CaP shows the highest bulk density of 3.198 g/cc.

Figure 4 shows, the apparent porosity distribution of the sintered calcium phosphate alumina composite with 5, 10 and 20% weight of CaP nano powder and Ca/P molar ratio i.e. 1.8, 1.67, 1.5, 1.33, 1.2 and 1.1.

The lowest apparent porosity corresponds respectively for samples with, 95 weight % alumina versus Ca:P molar ratio of 1.67, whose shows 11% AP, 90 weight % alumina versus Ca:P molar ratio of 1.2 with 13,75 AP and 80 weight % alumina versus Ca:P molar ratio of 1.67 whose apparent porosity is about 17%.







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Vickers hardness and bi-axial flexural strength

Vickers hardness measurements have been performed for a series of alumina-calcium phosphate composite compositions (Figure 5) shows the Vickers hardness distribution of (5% CaP- 95% Al_2O_3), (10% CaP- 90% Al_2O_3) and (20% CaP -80% Al_2O_3) sintered calcium phosphate –alumina composite (Table 2).

Composition with Ca:P molar ratio of 1.67 shows the highest hardness of 335 HV for the 5 weight % of CaP while the composition with Ca:P molar ratio of 1.2 shows the highest hardness of 287.8 HV for the 10% weight of CaP and composition with Ca:P molar ratio of 1.67 shows the highest hardness of 222.4 HV for the 20% weight of CaP [22].

Figures 6a-6d, show the load versus extension curve of 5% CaP(1.67)- 95% Al₂O₃, 10% CaP(1.67)- 90% Al₂O₃, 20% CaP(1.67)- 80% Al₂O₃ and 10% CaP(1.8)- 90% Al₂O₃ respectively .



Composite	Bi-Axial Flexural Strength (MPa)
5% CaP(1.67) 95% Al ₂ O ₃	47.545
10% CaP(1.8) 90% Al ₂ O ₃	23.23
10% CaP(1.67) 90% Al ₂ O ₃	24.14
20% CaP(1.67) 80% Al ₂ O ₃	19.84

Table 2: Bi-Axial Flexural strength of different sintered composites.









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The obtained results show that the composition of 5 wt% CaP (1.67) and 95 wt% Al_2O_3 has the highest Vicker's hardness of 335 HV and the highest flexural strength of 47.545 MPa. This is mainly due to bulk density and porosity properties (10).

Conclusion

Alumina–calcium phosphate composites with different Ca/P molar ratio and variation in weight % of Calcium phosphate and alumina from 5:95 to 20:80 were successfully processed and characterized [23]. The obtained results in our studies show that, the composition of 5 wt% CaP (1.67) and 95 wt% Al_2O_3 showed the highest bulk density of 3.76 g/cc, the lowest porosity of 11%, the highest Vickers's hardness of 335 HV and the highest flexural strength of 47.545 MPa. In order to complete investigation on use of such materials as implant an In-vitro bioactivity study using osteoblast cell line will be undertaken for all the alumina- calcium phosphate composites.

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