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Effect of B_2O_3 on mechanical properties of porous natural hydroxyapatite derived from cortical bovine bones sintered at 1,050˚C

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ABSTRACT

Due to its close physical and chemical properties to the mineral part of bone and teeth, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is one of the most attractive materials for human hard-tissue implants. However, its poor mechanical properties are one of the most serious obstacles for wider applications of hydroxyapatite. Optimizing the main parameters controlling a natural hydroxyapatite (NHA) production such as milling techniques, compacting pressure, sintering temperature, holding time and B_2O_3 additions may lead to better NHA-based bioceramics. Consequently, different percentages of B_2O_3 (0.5–5.0 wt.%) have been added to NHA powders in order to promote densification and to lower the sintering temperature of porous NHA. Afterwards, these powders were uniaxially cold compacted at 75 MPa and sintered at 1,050˚C for 2 h. The porosity ratio was ranged between 27 and 43%. The best Vickers micro-hardness value was 2.1 GPa (using 300 g). This value is much higher than those of NHA (0.6–0.9 GPa) prepared using other usual techniques even with foreign oxide additions such as ZrO_2. As far as three point bending strength is concerned, a strength of about 57 MPa was also obtained using this proposed process. This value is significantly higher than that reported by others (35 MPa) using the sol–gel method.

Keywords: Natural hydroxyapatite; Mechanical properties; B_2O_3; Sintering

1. Introduction

Using raw materials instead of industrial chemicals in making ceramics is becoming more popular [1–3]. Algeria is one of the countries that has abundantly available raw materials such as calcite ($CaCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), bones (natural derived hydroxyapatite: $Ca_{10}(PO_4)_6(OH)_2$), kaolin, feldspar and quartz. Much work has already been published on improving these native raw materials. Studies have been published on advanced ceramics [1–3], ceramic membranes [4–10] and bioceramics [11–15]. In particular, calcite and dolomite coupled with highly pure SiO_2 were used for fabrication of highly resistant wollastonite ($CaSiO_3$)-based [13] and diopside

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($CaMgSi_2O_6$)-based [14] bioceramics, respectively. A great potential exists for the use of natural hydroxyapatite (NHA) as a raw material for porous hydroxyapatite-based ceramics as membrane supports. Ceramics filters are generally constituted of a thick support (2,000 μm) and mono or multi thin membranes (from 10 to 40 μm for each one). This work mainly focussed on the ceramic support rather than deposited membranes. Replacing the more expensive starting materials, mentioned above, by other cheaper raw materials used in supports (which constitute about 99% of the filter mass) is considerably important. So, what is meant by low-cost raw materials? For example, the alumina price is at least 100 times greater than that of kaolin. Another important advantage of mullite- and anorthite-based ceramics is the substantial saving in energy obtained by decreasing the sintering temperature from about 1,600 to about 1,250˚C [10], when alumina supports are replaced by the proposed supports. Also, about 50% of the support is porous. The relative lower theoretical density of the prepared supports ($2.8 g/cm^3$), when compared to that of alumina ($3.98 g/cm^3$), is another advantage. More recently, it has been demonstrated that the fabricated membrane supports have comparable mechanical strength to that of alumina [10]. Indeed, a flexural strength of 87 ± 2 MPa was obtained for 100 wt.% Al_2O_3 samples sintered at 1,620˚C for 2 h [16], whilst nearly the same flexural strength value (87 ± 6 MPa) was also measured for samples sintered at only 1,250˚C for 1 h, using the proposed process.

Due to its close physical and chemical properties to the mineral part of bone and teeth, hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) is one of the most attractive materials for human hard-tissue implants [17,18]. The biocompatibility of this ceramics is good enough that, when used as an implant material, it forms a direct bond with neighbouring bone. Nevertheless, its poor mechanical properties compared to that of other resistant ceramics [19,20] are one of the most serious obstacles for wider applications [21–34]. Hence, there has been much effort to improve the mechanical properties of hydroxyapatite by introducing foreign oxides or metallic dispersions as reinforcing agents [21,22]. Amongst them, zirconia (ZrO_2) and alumina (Al_2O_3) additions have been found to produce high mechanical strength and toughness without degrading the biocompatibility of hydroxyapatite samples [22–26]. Hydroxyapatite–zirconia composites have shown improved strength and toughness as compared to monolithic hydroxyapatite alone [27–32]. In addition, TiO_2 was used as a reinforcing phase of hydroxyapatite and tri-calcium phosphate (TCP) [18]. Nevertheless, when foreign oxides are used as a reinforcing agent for hydroxyapatite, the decomposition of hydroxyapatite to TCP occurs severely [21–23]. In fact, this decomposition had a negative influence on both densification and mechanical properties of hydroxyapatite because of the second phase formation and water steam [21,22,30,34]. Generally, membrane supports should have a total porosity ratio of about 45% as reported in the literature [4,10]. According to earlier results, there is a relationship between porosity ratio, pore sizes, sintering temperatures and mechanical properties [10]. Since porous supports should resist the applied pressure during solution filtrations, a higher mechanical strength is also of a great significance.

Therefore, in order to avoid these drawbacks, oxide addition such as B_2O_3 is a good option. There has been much effort to improve the mechanical properties of hydroxyapatite by introducing foreign oxides or metallic dispersions as reinforcing agents. Amongst previous studies, a simple and energetically vibratory multidirectional milling system using bimodal distribution of highly resistant ceramics has been used for obtaining sub-micron-sized NHA powders [35]. Optimizing the main parameters controlling NHA production such as milling techniques, compacting pressure, sintering temperature, holding time and B_2O_3 additions may lead to better NHA-based bioceramics.

In this study, B_2O_3 was added to NHA in order to improve its poor mechanical strength. In order to promote the densification and to lower the sintering temperature of porous NHA, different percentages of B_2O_3 (0.5–5.0 wt.%) were added to NHA powders, similarly to [13]. Indeed, the addition of B_2O_3 to NHA has substantially enhanced its mechanical strength. It has been found that the relative density of wollastonite samples is closely related to both sintering temperatures and B_2O_3 addition. By the addition of B_2O_3, sintering temperature was lowered by about 250˚C (from 1,300 to 1,050˚C), because melting of calcium borate helps sintering of wollastonite ceramics. A relative density higher than 97% of the theoretical one was reached for samples sintered at only 1,050˚C and containing 5 wt.% B_2O_3. An excellent 3-point bending strength value (343 ± 32 MPa) for samples containing 5 wt.% B_2O_3 was obtained. Moreover, a bending strength of 351 ± 27 MPa was obtained for Al_2O_3 samples containing 5.0 wt.% Cr_2O_3 and sintered at 1,600˚C for 1 h [20], whilst nearly the same bending strength value (343 ± 32 MPa) was also measured for $CaSiO_3$ ceramics containing 5 wt.% B_2O_3, sintered at 1,050˚C for 2 h, using the proposed process. This result clearly shows the importance of the obtained value of bending strength when compared (within the error bars) to one of the most resistant ceramics (corundum-based refractories). In fact, these interesting bending strength values are of great importance for many bioceramics applications.

2. Experimental procedure

2.1. Preparation of specimens

The starting material, used in this work, was NHA obtained by calcination of cortical bovine bone at 800˚C for 4 h to remove any organic material. After that, the calcined bone was dry-milled for 30 min. Series of pure NHA powders and powders containing different percentages of B_2O_3 (0.5–5.0 wt.%) were wet-milled for different times, using a homemade particular vibratory milling set-up [35]. Afterwards, samples were dried and compacted at 75 MPa under cold pressing. Subsequently, the compacted samples were sintered at 1,050˚C for 2 h. The bulk density was determined using Archimedes method.

2.2. Characterizations

The tensile strength of sintered specimens was obtained using a diametral compression test (FORM TEST SEIDNER D 79-40) (Germany). One of the fundamental aspects of this test is the relatively small proportion of the specimen volume which reaches the peak stress at fracture.

In its simplest form, a right circular cylindrical specimen is diametrally compressed between two flat platens. A biaxial stress state is produced within the test specimen, and on the assumption of an ideal line loading, the vertical plane is subjected to a uniform horizontal tensile strength of magnitude σ_t.

$$\sigma_t = 2P/\pi dt \tag{1}$$

where σ_t (MPa) is the maximum tensile stress, P (N) is the applied load at fracture, d (mm) is the specimen diameter, and t (mm) is the specimen thickness.

The relationship between measured tensile strength (σ_t) and its equivalent 3-point flexural (bending) strength (σ_f) is given by the following equation:

$$\sigma_f \text{ (MPa)} = 2.7\sigma_t \text{ (MPa)} \tag{2}$$

Eq. (2) was also confirmed by Harabi [36]. It should be noted that the flexural strength is needed for comparison purpose since it is generally used by most investigators. Hundreds of samples within the two different shapes have been tested separately. It has been confirmed that the conversion ratio between flexural strength and tensile strength of samples is identical. Vickers hardness values were measured with a micro-hardness testing machines (Leitez Wetzlar 6844) (Germany). All the values presented are the average of at least three specimens. Phase compositions of prepared samples were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) (Karlsruhe, Germany) with a CuKα radiation ($\lambda = 0.154$ nm) and a Ni filter, with working voltage 40 kV and working current 30 mA. The microstructure of each milled NHA powder was observed using a SEM (HITACHI, JSM-6301 F) (Tokyo, Japan) working at a 15 kV as an accelerating voltage. Before SEM observation, all samples were gold coated.

3. Results and discussion

Fig. 1 shows typical sub-micron-sized NHA powders obtained using a vibratory multidirectional milling system [35]. This micrograph illustrates that the milled NHA powder is transformed to homogeneous sub-micron-sized spherical particles or crystals. Moreover, the NHA structure was also confirmed by XRD as shown in Fig. 2. All peaks shown in this figure belong only to hydroxyapatite.

The variation of Vickers micro-hardness as a function of B_2O_3 percentage (wt.%) for samples sintered at 1,050˚C for 2 h is shown in Fig. 3. As would be expected, the relatively lower Vickers micro-hardness values (0.45–0.60 GPa) at 3 wt.% B_2O_3 increased sharply (2.1 GPa). Indeed, the Vickers micro-hardness

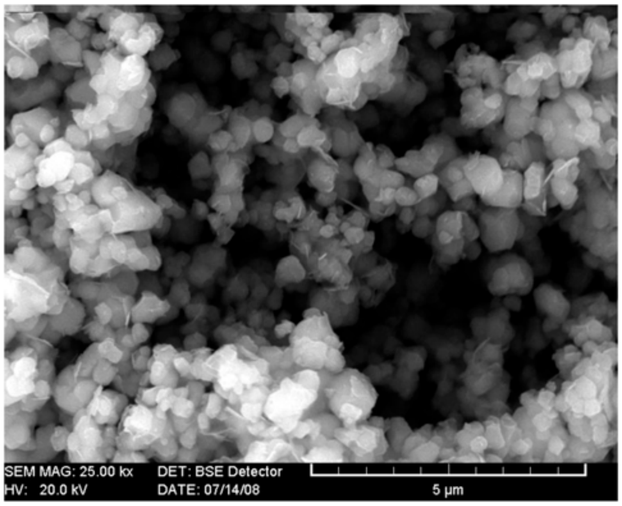

Fig. 1. SEM micrograph showing typical sub-micron-sized NHA powders obtained using a vibratory multidirectional milling system.

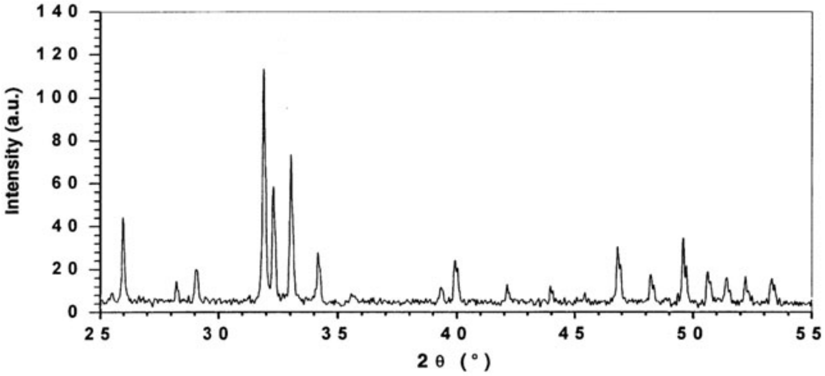

Fig. 2. XRD spectrum of NHA powder, calcined at 800˚C for 4 h.

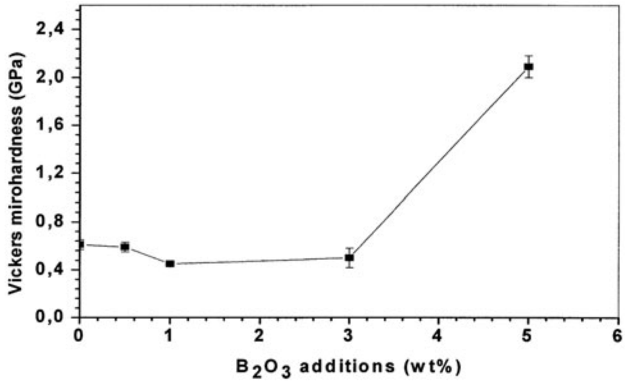

Fig. 3. Vickers micro-hardness as function of wt.% B_2O_3 for samples sintered at 1,050˚C for 2 h.

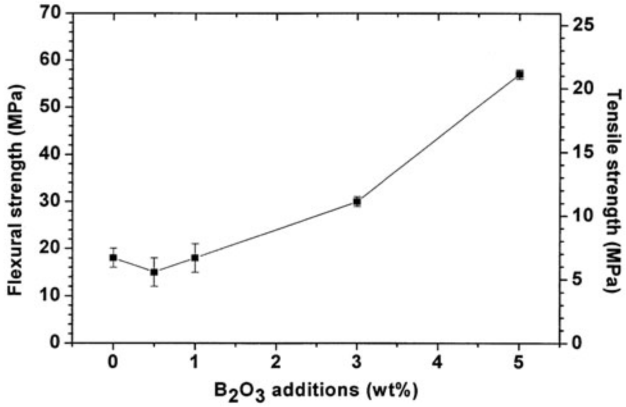

Fig. 4. Tensile strength as function of B_2O_3 percentages (wt.%) for samples sintered at 1,050˚C for 2 h.

values behaviour is in good agreement with the corresponding porosity ratio values. The effect of B_2O_3 addition (wt.%) on three-point flexural strength for samples sintered at 1,050˚C for 2 h is shown in Fig. 4. This curve displays that both Vickers micro-hardness and flexural strength behave, more or less, similarly. A comparison between mechanical properties values of the prepared materials in this study and those reported in the literature [36–42] is shown in Table 1. A correlation appears to exist between densification, micro structural changes (average grain size, phase type, pore distribution and total porosity) and tensile (or flexural) strength in sintered compacts. Usually, densification and grain size are the dominant factors controlling strength, since most of the total pores were intergranular. The significant increase in strength of samples corresponded to a parallel increase in density which means a decrease in porosity ratio [21,23,25].

Beneficially, the flexural strength value is significantly higher than that reported by others on similar based ceramics [36–43]. This value of 57 ± 1 MPa is also significantly higher than that reported by Sarkar et al. [40] (41 MPa), Bouzerara et al. [4,42] (41 MPa) and Dong et al. [43] (36 MPa) for their membrane supports, although some of them have been sintered at higher temperatures (≥1,450˚C). A flexural strength of 57 ± 6 MPa was obtained for yttria-stabilized ZrO_2 samples sintered at 1,450˚C for 2 h [41], whilst nearly the same flexural strength value (57 ± 1 MPa) was also measured for compacts sintered only at 1,050˚C for 1 h, using the milling system of the current study. Another good example is the better three-point flexural strength value (about 55.4 MPa) recently obtained by Chang et al. [39] for coarse Al_2O_3 porous supports containing nano-sized TiO_2 powder and sintered at 1,650˚C for 2 h. One can notice that this three-point flexural strength value (about 55.4 MPa) was slightly better, within the error bars, than that obtained in this work (57 ± 1 MPa) for NHA containing 5 wt.% B_2O_3 powders sintered at only about 1,050˚C for 2 h. Flexural strength is of great importance for porous membrane supports as well as porous ceramics.

Table 1
Comparison between mechanical properties values of the prepared materials in this study and those reported in the literature [38–41]

Material	Temperature (°C)	Porosity (%)	Flexural strength (MPa)	Vickers hardness (GPa)	References
NHA	1,050	36.4	18 ± 2	0.61 ± 0.04	Present work
NHA+0.5 wt% B_2O_3	1,050	41.4	15 ± 3	0.59 ± 0.04	
NHA + 1.0 wt.% B_2O_3	1,050	42.7	18 ± 3	0.45 ± 0.01	
NHA + 3.0 wt.% B_2O_3	1,050	43.3	30 ± 1	0.50 ± 0.08	
NHA + 5.0 wt.% B_2O_3	1,050	27.2	57 ± 1	2.09 ± 0.09	
NHA	1,300	3	–	0.61	[37]
NHA + 5.0 wt.% Zr_2O_2	1,300	5	–	0.94	
NHA + 5.0 wt.% TiO_2	1,300	10	–	0.67	
NHA + 5.0 wt.% Al_2O_3	1,300	3	–	0.69	
HA	1,250	4	35	–	[38]
HA + 2 wt.% ZrO_2	1,250	–	70	–	
Kaolin + 15wt% Doloma	1,250	41	41	–	[4,39]
Nano-TiO_2-coated Porous Al_2O_3	1,650	38	55.4	–	
Kaolin + 45 wt.% Al_2O_3	1,450	44	40	–	[40]
Kaolin + 30 wt.% Al_2O_3	1,450	40	56	–	
Yttria-stabilized ZrO_2	1,450	51.3	57	–	[41]
Bauxite + 6 wt. TiO_2	140	43	36	–	[43]

In order to simulate the multiaxial loads and stresses imposed upon ceramics under actual service conditions, new techniques have been developed to gain practical tensile strength data for use in design calculations. Amongst these are the multiaxial loading of thin-walled ceramic tubes, equibiaxial tension tests, the theta test, indentation, torsion and diametral compression of rings or discs [10]. These multiaxial strength tests appear to be more remarkable since they seem to take into account the effects of multiaxial loading. Nevertheless, one major problem with these tests is that they do not show a homogeneous state of stress since the maximum tensile stress at the zone of failure drops off rapidly to a lower level. However, some of these multiaxial stress tests have advantages such as the diametral compression test. It has the benefit of low economic cost. Thus, the surface finish of specimen is not a critical factor. The commonly observed modes of failure can be classified into three distinct types: (A) normal tension, (B) triple-cleft and (C) compression and shear as well documented elsewhere [10]. It should be noted that the corresponding tensile strength values increased sharply from A to C failure modes [10]. That is why, in this study, the disc configuration was preferred to the tubular one [10]. Unfortunately, many compositions or samples have been discarded without any strength measurements, just because their failure modes were of A type (poor values). Nevertheless, more detailed studies have been carried out on samples having B- and/or C-type failure modes, like in this work. Additionally, it should be mentioned that the process used in this work is much easier than others used for bioactive glass-based ceramics preparation [44,45]. Finally, it should also be remarked here that using ceramics (oxides) [46] instead of metallic products [47,48] is well justified, particularly for water filtration.

4. Conclusions

Different percentages of B_2O_3 (0.5–5.0 wt.%) have been added to NHA powders. The porosity ratio of NHA with B_2O_3 (0.5–5.0 wt.%) ranged between 27 and 43%. The best Vickers micro-hardness value was 2.1 GPa (using 300 g). This value was much higher than that of NHA (0.6–0.9 GPa) prepared using conventional techniques even with foreign oxide such as ZrO_2. As far as the three-point bending strength is concerned, a strength of about 57 MPa was obtained using this new milling system. This value is significantly higher than that reported by others (35 MPa) using the sol–gel method. These excellent mechanical properties were obtained using an improved milling system and by adding B_2O_3 (0.5–5.0 wt.%) to NHA powders.

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References

[1] A. Harabi, S. Achour, A process for sintering of MgO and CaO based ceramics, J. Mater. Sci. Lett. 18 (1999) 955–957.
[2] M.R. Boudchicha, S. Achour, A. Harabi, Crystallisation and sintering of cordierite and anorthite based binary ceramics, J. Mater. Sci. Lett. 20 (2001) 215–217.
[3] A. Mecif, J. Soro, J.P. Bonnet, A. Harabi, Preparation of mullite and zircon based ceramics using kaolinite and zirconium oxide: A sintering study, J. Am. Ceram. Soc. 93 (2010) 1306–1312.
[4] F. Bouzerara, A. Harabi, S. Achour, A. Larbot, Porous ceramic supports for membranes prepared from kaolin and doloma mixtures, J. Eur. Ceram. Soc. 26 (2006) 1663–1671.
[5] A. Harabi, F. Bouzerara, S. Condom, Preparation and characterization of tubular membrane supports using centrifugal casting, Desalin. Water Treat. 6 (2009) 222–226.
[6] B. Boudaira, A. Harabi, F. Bouzerara, S. Condom, Preparation and characterization of microfiltration membranes and their supports using kaolin (DD2) and $CaCO_3$, Desalin. Water Treat. 9 (2009) 142–148.
[7] F. Bouzerara, A. Harabi, S. Condom, Porous ceramic membranes prepared from kaolin, Desalin. Water Treat. 12 (2009) 415–419.
[8] A. Harabi, A. Guechi, S. Condom, Production of supports and filtration membranes from algerian kaolin and limestone, Procedia Eng. 33 (2012) 220–224.
[9] F. Bouzerara, A. Harabi, B. Ghouil, N. Medjemem, B. Boudaira, S. Condom, Synthesis and characterization of multilayer ceramic membranes, Procedia Eng. 33 (2012) 78–84.
[10] A. Harabi, F. Zenikheri, B. Boudaira, F. Bouzerara, A. Guechi, L. Foughali, A new and economic approach to fabricate resistant porous membrane supports using kaolin and $CaCO_3$, J. Eur. Ceram. Soc. 34 (2014) 1329–1340.
[11] F.Z. Mezahi, H. Oudadesse, A. Harabi, A. Lucas-Girot, Y. Le Gal, H. Chaair, G. Cathelineau, Dissolution kinetic and structural behaviour of natural hydroxyapatite vs. thermal treatment, J. Therm. Anal. Calorim. 95 (2009) 21–29.
[12] F.Z. Mezahi, H. Oudadesse, A. Harabi, Y. Gal, Effect of ZrO_2, TiO_2, and Al_2O_3 additions on process and kinetics of bonelike apatite formation on sintered natural hydroxyapatite surfaces, Int. J. Appl. Ceram. Technol. 9 (2012) 529–540.
[13] A. Harabi, S. Chehlatt, Preparation process of a highly resistant wollastonite bioceramics using local raw materials, J. Therm. Anal. Calorim. 111 (2013) 203–211.
[14] A. Harabi, S. Zouai, A new and economic approach to synthesize and fabricate bioactive diopside ceramics using a modified domestic microwave oven. Part 1: Study of sintering and bioactivity, Int. J. Appl. Ceram. Technol. 11 (2014) 31–46.
[15] A. Harabi, D. Belamri, N. Karboua, F.Z. Mezahi, Sintering of bioceramics using a modified domestic microwave oven: Natural hydroxyapatite sintering, J. Therm. Anal. Calorim. 104 (2011) 283–289.
[16] Y. Dong, B. Lin, J. Zhou, X. Zhang, Y. Ling, X. Liu, G. Meng, S. Hampshire, Corrosion resistance characterization of porous alumina membrane supports, Mater. Charact. 62 (2011) 409–418.
[17] F.Z. Mezahi, H. Oudadesse, A. Harabi, A. Lucas-Girot, Y. Le Gal, H. Chaair, G. Cathelineau, Dissolution kinetic and structural behaviour of natural hydroxyapatite vs. thermal treatment, J. Therm. Anal. Calorim. 95 (2009) 21–29.
[18] A. Harabi, D. Belamri, N. Karboua, F.Z. Mezahi, Sintering of bioceramics using a modified domestic microwave oven: Natural hydroxyapatite sintering, J. Therm. Anal. Calorim. 104 (2011) 283–289.
[19] A. Harabi, T.J. Davies, Densification and grain growth in sintered alumina-chromia powder mixtures, Br. Ceram. Trans. J. 94(2) (1995) 79–84.
[20] A. Harabi, T.J. Davies, Mechanical properties of sintered alumina–chromia refractories, Br. Ceram. Trans. J. 94(3) (1995) 97–102.
[21] Y.M. Kong, S. Kim, H.E. Kim, Reinforcement of hydroxyapatite bioceramic by addition of ZrO_2 coated with Al_2O_3, J. Am. Ceram. Soc. 82(11) (1999) 2963–2968.
[22] R. Ramachandra Rao, T.S. Kannan, Synthesis and sintering of hydroxyapatite–zirconia composites, Mater. Sci. Eng. 20(1–2) (2002) 187–193.
[23] V.V. Silva, F.S. Lameiras, R.Z. Domingues, Microstructural and mechanical study of zirconia-hydroxyapatite (ZH) composite ceramics for biomedical applications, Compos. Sci. Technol. 61(2) (2001) 301–310.
[24] E. Champion, S. Gautier, D. Bernache-Assollant, Characterization of hot pressed Al_2O_3-platelet reinforced hydroxyapatite composites, J. Mater. Sci. Mater. Med. 7(2) (1996) 125–130.
[25] T. Kokubo, H.M. Kim, M. Kawashita, Novel bioactive materials with different mechanical properties, Biomaterials 24 (2003) 2161–2175.
[26] L.M. Epure, S. Dimitrievska, Y. Merhi, L.H. Yahia, The effect of varying Al_2O_3 percentage in hydroxyapatite/Al_2O_3 composite materials: Morphological, chemical and cytotoxic evaluation, J. Biomed. Mater. Res. (A), 83 A(4) (2007) 1009–1023.
[27] J. Zhang, M. Iwasa, N. Kotobuki, T. Tanaka, M. Hirose, H. Ohgushi, D Jiang, Fabrication of hydroxyapatite? Zirconia composites for orthopedic applications, J. Am. Ceram. Soc. 89(11) (2006) 3348–3355.
[28] K.A. Khalil, S.W. Kim, H.Y. Kim, Consolidation and mechanical properties of nanostructured hydroxyapatite-(ZrO_2+3mol% Y_2O_3) bioceramics by high-frequency induction heat sintering, Mater. Sci. Eng. A 456(1–2) (2007) 368–372.
[29] A. Rapacz-Kmita, A. Ślósarczyk, Z. Paszkiewicz, Mechanical properties of HAp–ZrO_2 composites, J. Eur. Ceram. Soc. 26 (2006) 1481–1488.
[30] J.M. Wu, T.S. Yeh, Sintering of hydroxylapatite-zirconia composite materials, J. Mater. Sci. 23 (1988) 3771–3777.
[31] Z. Evis, M. Usta, I. Kutbay, Hydroxyapatite and zirconia composites: Effect of MgO and MgF_2 on the

stability of phases and sinterability, Mater. Chem. Phys. 110 (2008) 68–75.

[32] J. Suwanprateeb, R. Sanngam, W. Suvannapruk, T. Panyathanmaporn, Mechanical and *in vitro* performance of apatite–wollastonite glass ceramic reinforced hydroxyapatite composite fabricated by 3D-printing, J. Mater. Sci. Mater. Med. 20 (2009) 1281–1289.

[33] K.S. Oh, F. Caroff, R. Famery, M.F. Sigot- Luizard, P. Boch, Preparation of TCP–TiO_2 biocomposites and study of their cytocompatibility, J. Eur. Ceram. Soc. 18 (13) (1998)1931–1937.

[34] H.W. Kim, Y.J. Noh, Y.H. Koh, H. Kim, H.M. Kim, Effect of CaF_2 on densification and properties of hydroxyapatite-zirconia composites for biomedical applications, Biomaterials 23(20) (2002) 4113–4121.

[35] A. Harabi, A simple and energetically vibratory multidirectional milling system using bimodal distribution of highly resistant ceramics: Applied on hydroxyapatite derived from natural cortical bones, Patent, 13 pages, INAPI, No. 130393. ALGERIA, June 24th 2013.

[36] A. Harabi, Studies of an alumina–chromia system containing mullite, PhD Thesis, Manchester Materials Science Centre, UMIST, Manchester, 1990.

[37] F.Z. Mezahi, A. Harabi, S. Zouai, S. Achour, D. Bernache- Assollant, Effect of stabilised ZrO_2, Al_2O_3 and TiO_2 on sintering of hydroxyapatite, Mater. Sci. Forum. 492–493 (2005) 241–248.

[38] Y. Nayak, R.P. Rana, S.K. Pratihar, S. Bhattacharyya, Pressureless sintering of dense hydroxyapatite–zirconia composites, J. Mater. Sci. 19 (2008) 2437–2444.

[39] Q. Chang, Y. Wang, S. Cerneaux, J. Zhou, X. Zhang, X. Wang, Y. Dong, Preparation of microfiltration membrane supports using coarse alumina grains coated by nano TiO_2 as raw materials, J. Eur. Ceram. Soc. 34 (2014) 4355–4361.

[40] S. Sarkar, S. Bandyopadhyay, A. Larbot, S. Cerneaux, New clay–alumina porous capillary supports for filtration application, J. Membr. Sci. 392–393 (2012) 130–136.

[41] S. Kroll, L. Treccani, K. Rezwan, G. Grathwohl, Development and characterisation of functionalised ceramic microtubes for bacteria filtration, J. Membr. Sci. 365 (2010) 447–455.

[42] F. Bouzerara, S. Boulanacer, A. Harabi, Shaping of microfiltration (MF) ZrO_2 membranes using a centrifugal casting method, Ceram. Int. 41 (2015) 5159–5163.

[43] Y. Dong, S. Hampshire, J. Zhou, B. Lin, Z. Ji, X. Zhang, G. Meng, Recycling of fly ash for preparing porous mullite membrane supports with titania addition, J. Hazard. Mater. 180 (2010) 173–180.

[44] A. Lucas-Girot, F. Z. Mezahi, M. Mami, H. Oudadesse, A. Harabi, M. Le Floch, Sol-gel synthesis of a new composition of bioactive glass in the quaternary system SiO_2–CaO–Na_2O–P_2O_5. Comparison with melting method, J. Non-Cryst. Solids 357 (2011) 3322–3327.

[45] F.Z. Mezahi, A. Girot, Reactivity kinetics of 52S4 glass in the quaternary system SiO_2–CaO–Na_2O–P_2O_5: Influence of the synthesis process: Melting versus sol–gel, J. Non-Cryst. Solids 361 (2013) 111–118.

[46] S. Kitouni, A. Harabi, Sintering and mechanical properties of porcelains prepared from algerian raw materials, Cerâmica 57 (2011) 453–460.

[47] S.E. Barama, A. Harabi, G. Cizeron, Identification of intermetallic compounds formed during sintering of the Fe-Mo-W ternary system, J. Mater. Sci. Lett. 16 (1997) 1240–1244.

[48] S.E. Barama, A. Harabi, G. Cizeron, Processes involved during the production of Fe–W–Mo alloys by powder metallurgy, J. Mater. Sci. 33 (1998) 2431–2440.