Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1022000

57 (2016) 5297–5302
March

Taylor & Francis
Taylor & Francis Group

Effect of P_2O_5 on mechanical properties of porous natural hydroxyapatite derived from cortical bovine bones sintered at 1,050˚C

Esma Harabi*, Abdelhamid Harabi, Fatima-Zohra Mezahi, Souheila Zouai, Nour-Eddinne Karboua, Sihem Chehlatt

Ceramics Lab., Faculty of Exact Science, Physics Department, Constantine University 1, Constantine 25000, Algeria, Tel./Fax: +21331811126; emails: eharabi84@gmail.com (E. Harabi), harabi52@gmail.com (A. Harabi), mezahif@yahoo.fr (F.-Z. Mezahi), zouaisouheila@yahoo.fr (S. Zouai), kanour17@yahoo.fr (N.-E. Karboua), sihemcha@yahoo.fr (S. Chehlatt)

Received 12 February 2014; Accepted 12 October 2014

ABSTRACT

In the current study, the effect of P_2O_5 on the mechanical properties of porous natural hydroxyapatite (NHA) derived from cortical bovine bones sintered at 1,050˚C is assessed. Hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$) was synthesized using several methods and manufactured from natural materials such as coral or bone after removal of the organic matter by heating (noted NHA). The *in vitro and in vivo* studies showed that the natural apatite was well tolerated and has better osteoconductive properties than synthetic HA. Consequently, the NHA was manufactured from cortical bovine bone in all our studies. Nevertheless, its poor mechanical properties are one of the most serious obstacles for wider applications. So, P_2O_5 was added into NHA in order to enhance its initially poor mechanical strength. A careful combination between the main parameters controlling NHA elaboration such as milling techniques, compacting pressure, sintering temperature, and holding time may lead to an interesting NHA-based bioceramics. In this way, a vibratory multidirectional milling system using bimodal distribution of highly resistant ceramics has been used for obtaining submicron-sized NHA powders. To enhance the densification and lower the sintering temperature of porous NHA, different percentages of P_2O_5 (0.5–5.0 wt%) were added into NHA powders. The porosity ratio ranged between 36 and 41%. Using this modified milling system, the best Vickers micro-hardness and the three-point bending strength values of powders sintered at 1,050˚C were 1 GPa and about 46 MPa, respectively. The latter value is significantly higher than that reported by other researchers (35 MPa) using the sol–gel method.

Keywords: Natural hydroxyapatite; Mechanical properties; Sintering; P_2O_5

*Corresponding author.

Presented at the International Conference on Water and Energy (ICW'13) Chlef University, Algeria, 16–17 December 2013

1. Introduction

Because of 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 [1–3]. The biocompatibility of this ceramic, when used as an implant material, is good enough to form a direct bond with the neighboring bone. Nevertheless, its poor mechanical properties are one of the most serious obstacles for wider applications [4]. Consequently, there has been much effort to improve the mechanical properties of HA by introducing foreign oxides or metallic dispersions as reinforcing agents [5–7]. Among them, the addition of zirconia (ZrO_2) and alumina (Al_2O_3) has been found to improve the mechanical strength and toughness of HA without degrading its biocompatibility [7–11]. HA–zirconia composites have shown improved strength and toughness as compared to monolithic HA itself [12–17]. In addition, TiO_2 was used as a reinforcing phase for HA and tri-calcium phosphate (TCP) [18]. By contrast, when foreign oxides are used as a reinforcing agent for HA, the decomposition of HA to TCP occurs [5–8]. In fact, this decomposition had a negative influence on both sintering and mechanical properties of HA because of the second phase formation and water steam [5–7,15,19].

Also, there has been much effort to improve the mechanical properties of HA by introducing specific foreign oxides as reinforcing agents, especially when porous natural hydroxyapatite (NHA) was used as ceramic membranes for solution filtration or injection inside human bodies. So, P_2O_5 was added to NHA in order to enhance its mechanical strength. A careful combination between the main parameters controlling NHA production such as milling techniques, compacting pressures, sintering temperatures, and holding times may lead to NHA-based bioceramics. In this way, a vibratory multidirectional milling system using bimodal distribution of highly resistant ceramics has been used for obtaining submicron-sized NHA powders [20]. In order to promote densification and lower the sintering temperature of porous NHA, different percentages of P_2O_5 (0.5–5.0 wt%) were added into NHA powders. Many works have already been published for increasing the value of calcite ($CaCO_3$), dolomite ($CaCO_3{\cdot}MgCO_3$), bones (natural derived hydroxyapatite: HA: $Ca_{10}(PO_4)_6(OH)_2$), kaolin, feldspar, and quartz native raw materials. These topics concern advanced ceramics [21–23], ceramic membranes [24–30], and bioceramics [31–37]. For instance, calcite and dolomite coupled with highly pure SiO_2 were also used for fabrication of highly resistant wollastonite ($CaSiO_3$)-based [33] and diopside ($CaMgSi_2O_6$)-based [34] bioceramics, respectively. Therefore, an attempt has been dictated in order to use NHA abundantly available as a local raw material for porous NHA-based ceramics production.

The aim of the current work was to study the effect of P_2O_5 additions on the mechanical properties of porous NHA derived from cortical bovine bones sintered at 1,050˚C.

2. Experimental procedures

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 out the organic matter. After that, the calcined bone was dry milled for 30 min. Series of pure NHA powders and other powders containing different percentages of P_2O_5 (0.5–5.0 wt%) were wet milled for different times, using a modified vibratory multidirectional milling setup [20]. Then, they 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 testing 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 compressed diametrally between two flat platens. A biaxial stress state is produced within the test specimen, and on the assumption of ideal line loading, the vertical plane is subjected to a uniform horizontal tensile strength given by Eq. (1).

$$\sigma_t = 2P/\pi \mathrm{d}t \tag{1}$$

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 correspondence between the measured tensile strength (σ_t) value and its equivalent three-point flexural (bending) strength (σ_f) is given by Eq. (2):

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

Eq. (2) was also confirmed by Harabi [38]. It should be noticed that the deduced flexural strength is

needed for comparison since it is generally used by the major investigators. Hundreds of samples with the two different shapes were tested separately. So, it has also been confirmed that the conversion ratio between flexural strength and tensile strength of samples is always interchangeable.

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, working voltage of 40 kV, and working current of 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 a typical submicron-sized NHA powder obtained using a vibratory multidirectional milling system. This original device was composed of 4 main parts: a metallic cylinder, a Teflon bottle, a motor, and a rotational system. The latter rotates the cylinder with a constant speed. In order to avoid the adhesion of the powder on its sides, the bottle has been placed oblically in the middle of the cylinder. This device is also composed of rigid flexible springs which make the bottle to vibrate powerfully. These last two properties are the cause of the multidirectional rotation. As a result, powerful and continuous collisions occur between the hard milling balls and the powder particles which substantially reduce the powder particle size. The third property concerns the utilization of two different milling balls sizes. The last property is the use of a liquid which in turn homogeneously disperses the powder particles and conserves the temperature of the bottle container lower.

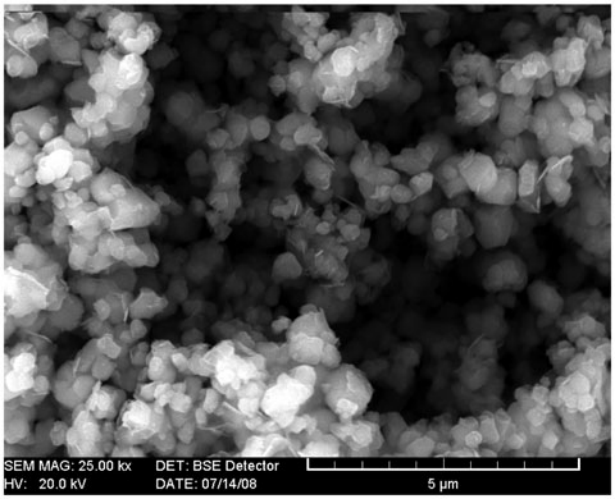

Fig. 1. SEM micrograph showing a typical submicron-sized NHA powder obtained using a vibratory multidirectional milling system.

The XRD shows that the initial calcined powder is HA (Fig. 2) with the following chemical composition: $Ca_{10}(PO_4)_6(OH)_2$. In addition, this spectrum shows also that the NHA powder is well crystallized (see Fig. 3).

The sintering temperature is an important parameter which controls the porosity. In this study, a low temperature (1,050˚C) was chosen, because the melting temperature of the addition is low and this may be the origin of the presence of an important amount of porosity ratio.

As would be expected, the Vickers micro-hardness variation fits well with the porosity variation (Table 1).

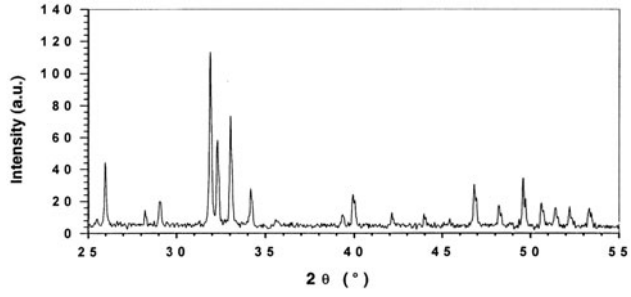

Fig. 2. XRD spectrum of NHA powder calcined at 800˚C for 4 h.

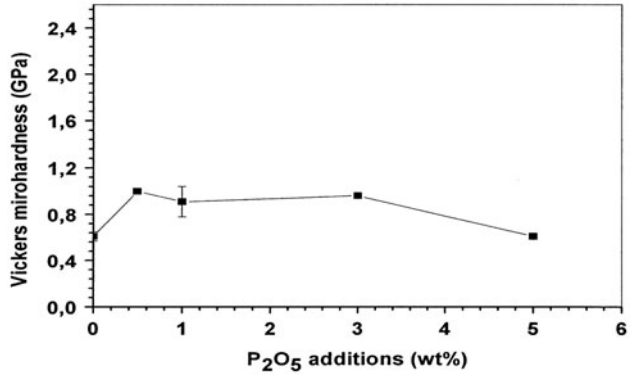

Fig. 3. Vickers micro-hardness as function of P_2O_5 percentages (wt%) for samples sintered at 1,050˚C for 2 h. Apart from 1 wt% P_2O_5, the other error bars were not visible in this figure because of their lower values.

The best Vickers micro-hardness value was 1.0 GPa (using 300 g). This value is slightly higher than that for NHA (0.6–0.9 GPa) prepared with foreign oxides such as ZrO_2 [39].

As far as the three-point bending strength is concerned, a strength of about 46 MPa was also obtained using this proposed process (Fig. 4). This value is significantly higher than that reported by other investigators (i.e. 35 MPa) using the sol–gel method.

As illustrated in Table 1, the porosity ratio ranged between 36 and 42%, and the porosity increases when the addition percentage increases as well. This increase in porosity may be due to the addition of lower melting temperature oxides. Moreover, Table 1 summarizes a comparison between mechanical properties values of the porous HA materials prepared in this study and for those reported in the literature [39–44]. From a careful examination of this table, one can notice the importance of these prepared porous products only when 3–5 wt% P_2O_5 was applied. For example, the best flexural strength value in this work (46 MPa) is slightly higher than that (41 MPa) reported in Ref. [42] for kaolin + 45 wt% Al_2O_3 compacts although they were sintered at 1,450˚C. Another good example is the best three-point flexural strength value (about 55.4 MPa) recently obtained by Chang et al. [41] 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 comparable within the error bars to that obtained in this work (46 ± 8 MPa) for NHA containing 3 wt% P_2O_5 powders sintered at only about 1,050˚C for 2 h.

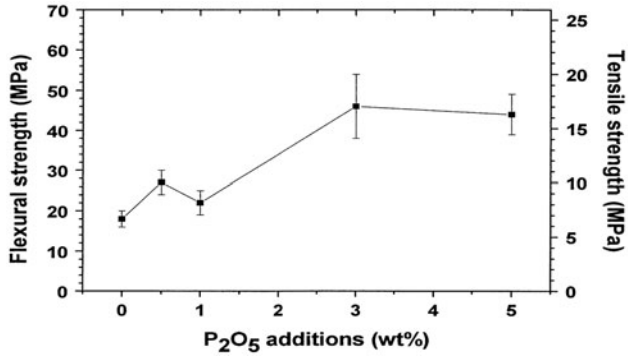

Fig. 4. Tensile strength as function of P_2O_5 percentages (wt%) for samples sintered at 1,050˚C for 2 h.

The beneficial effect of this proposed milling system coupled with P_2O_5 additions on the mechanical properties of samples sintered only at 1,050˚C is clearly evident in Table 1.

Moreover, the relatively higher porosity ratios (36–42%) of these porous bioceramics may also qualify them to be used as membrane supports. This

Table 1
Comparison between mechanical properties of NHA containing P_2O_5 prepared in this study and those reported in the literature [39–44]

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% P_2O_5	1,050	38.8	27 ± 3	1.00 ± 0.01	
NHA + 1.0 wt% P_2O_5	1,050	41.7	22 ± 3	0.91 ± 0.13	
NHA + 3.0 wt% P_2O_5	1,050	37.4	46 ± 8	0.96 ± 0.01	
NHA + 5.0 wt% P_2O_5	1,050	41.4	44 ± 5	0.61 ± 0.01	
NHA	1,300	3	–	0.61	[39]
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	–	[40,41]
Nano-TiO_2 coated Porous Al_2O_3	1,650	38	55.4	–	
Kaolin + 15 wt% Doloma	1,200	41	41	–	[24]
	1,250	41	41	–	
Kaolin + 45 wt% Al_2O_3	1,450	44	40	–	[42]
Kaolin + 30 wt% Al_2O_3	1,450	40	56	–	
Ytria stabilized ZrO_2	1,450	51.3	57	–	[43]
Bauxite + 6 wt% TiO_2	1,450	43	36	–	[44]

further application is also motivated by some results summarized in Table 1. Indeed, a preliminary study carried out on these porous NHA samples sintered at 1,050°C showed that their pore size distribution was homogeneous (Gaussian) within around 0.4 μm as an average pore size.

Additionally, it should be noticed that the proposed process used in this work is much easier than the others used for bioactive glass-based ceramics preparation [36,37]. It should also be mentioned here that using ceramics (oxides) in this work and others [45] instead of metallic products [46,47] is well justified, particularly for used water filtration or purification.

All in all, it can be said that the proposed milling system does not only lower down the average particle size of powders but it also ameliorates the powder mixing especially when small additions have been used. This is in a good agreement with the results reported elsewhere [48–50].

4. Conclusions

The porosity ratio of NHA containing P_2O_5 ranged between 36 and 42%. The relatively higher porosity ratios of these bioceramics may qualify them to be used as membrane supports. The best Vickers microhardness value was 1.0 GPa (using 300 g). This value is slightly higher than those of NHA (0.6–0.9 GPa) prepared using other usual techniques even with foreign oxide additions such as ZrO_2. The three-point bending strength value was significantly higher than that reported by others (35 MPa) using the sol–gel method. These relatively excellent mechanical properties were obtained by combining both milling system and P_2O_5 (0.5–5.0 wt%) additions into NHA powders. Finally, it can be said that the milling system does not only lower the average particle size of powders but it also ameliorates powder mixing especially for small amount additions.

Acknowledgements

The authors gratefully acknowledge the partial financial support received from the DGRSDT [grant number 7/u250/823] and thank Prof. H. Ourag DGRSDT general director for equipment buying facilities (Hg Porosimeter, BET, and FTIR), Algeria.

References

[1] L.L. Hench, Bioceramics: From concept to clinic, J. Am. Ceram. Soc. 74 (1991) 1487–1510.
[2] 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.
[3] 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.
[4] L.L. Hench, J. Wilson (Eds.), Advanced Series in Ceramics: An Introduction of Bioceramics, vol. 1, World Scientific Publishing, Singapore, 1993, pp. 1–24.
[5] J. Huaxia, P.M. Marquis, Sintering behaviour of hydroxyapatite with 20 wt% of Al_2O_3, J. Mater. Sci. 28 (1993) 1941–1945.
[6] 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.
[7] R. Rao Ramachandra, T.S. Kannan, Synthesis and sintering of hydroxyapatite–zirconia composites, Mater. Sci. Eng. C20(1–2) (2002) 187–193.
[8] V.V. Silva, F.S. Lameiras, R.Z. Domingues, Microstructural and mechanical study of zirconia-hydroxyapatite (ZH) composite ceramics for biomedical application, Compos. Sci. Technol. 61(2) (2001) 301–310.
[9] 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.
[10] T. Kokubo, H.M. Kim, M. Masakazu Kawashita, Novel bioactive materials with different mechanical properties, Biomaterials 24 (2003) 2161–2175.
[11] 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) 83A(4) (2007) 1009–1023.
[12] 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.
[13] K.A. Khalil, S.W. Kim, H.Y. Kim, Consolidation and mechanical properties of nanostructured hydroxyapatite-(ZrO_2 + 3 mol% Y_2O_3) bioceramics by high-frequency induction heat sintering, Mater. Sci. Eng. A 456(1–2) (2007) 368–372.
[14] A. Rapacz-Kmita, A. Slosarczyk, Z. Paszkiewicz, Mechanical properties of HAp–ZrO_2 composites, J. Eur. Ceram. Soc. 26 (2006) 1481–1488.
[15] J.M. Wu, T.S. Yeh, Sintering of hydroxyapatite-zirconia composite materials, J. Mater. Sci. 23 (1988) 3771–3777.
[16] 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.
[17] 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.
[18] 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.

[19] H.W. Kim, Y.J. Noh, Y.H. Koh, H. Ee 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.
[20] 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, INAPI, No. 130393, Algeria, June 24, 2013, 13 pages.
[21] A. Harabi, S. Achour, A process for sintering of MgO and CaO based ceramics, J. Mater. Sci. Lett. 18 (1999) 955–957.
[22] 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.
[23] 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.
[24] F. Bouzerara, A. Harabi, S. Achour, A. Labrot, Porous ceramic supports for membranes prepared from kaolin and doloma mixtures, J. Eur. Ceram. Soc. 26 (2006) 1663–1671.
[25] A. Harabi, F. Bouzerara, S. Condom, Preparation and characterization of tubular membrane supports using centrifugal casting, Desalin. Water Treat. 6 (2009) 222–226.
[26] B. Boudaira, A. Hara.bi, F. Bouzerara, S. Condom, Preparation and characterization of microfiltration membranes and their supports using kaolin (DD2) and $CaCO_3$, Deslin. Water Treat. 9 (2009) 142–148.
[27] F. Bouzerara, A. Harabi, S. Condom, Porous ceramic membranes prepared from kaolin, Deslin. Water Treat. 12 (2009) 415–419.
[28] A. Harabi, A. Guechi, S. Condom, Production of supports and membranes filtration from kaolin and limestone, Procedia Eng. 33 (2012) 220–224.
[29] 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.
[30] 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) 1329–1329.
[31] 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.
[32] F.Z. Mezahi, H. Oudadesse, A. Harabi, A. Lucas-Girot, 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.
[33] A. Harabi, S. Chehlatt, Preparation process of a highly resistant wollastonite bioceramics using local raw materials. Effect of B_2O_3 additions on sintering and mechanical properties, J. Therm. Anal. Calorim. 111 (2013) 203–211.
[34] 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, J. Appl. Ceram. Technol. 11 (2014) 31–46.
[35] 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.
[36] 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.
[37] F.Z. Mezahi, A. Lucas-Girot, H. Oudadesse, A. Harabi, 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–ge, J. Non-Cryst. Solids 361 (2013) 111–118.
[38] A. Harabi, Studies of an alumina–chromia system containing mullite, Ph.D. Thesis, Manchester Materials Science Centre, UMIST, Manchester, 1990.
[39] 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.
[40] Y. Nayak, R.P. Rana, S.K. Pratihar, S. Bhattacharyya, Pressureless sintering of dense hydroxyapatite–zirconia composites, J. Mater. Sci. 19 (2008) 2437–2444.
[41] 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) 4355–4356.
[42] 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.
[43] 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.
[44] 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.
[45] S. Kitouni, A. Harabi, Sintering and mechanical properties of porcelains prepared from algerian raw materials, Cerâmica 57 (2011) 453–460.
[46] 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.
[47] S.E. Barama, A. Harabi, G. Cizeron, Processes involved during the elaboration of Fe–W–Mo alloys by powder metallurgy, J. Mater. Sci. 33 (1998) 2431–2440.
[48] A. Harabi, T.J. Davies, Densification and grain growth in sintered alumina–chromia powder mixtures, Br. Ceram. Trans. 94 (1995) 97–102.
[49] A. Harabi, T.J. Davies, Mechanical properties of sintered alumina–chromia refractories, Br. Ceram. Trans. 94 (1995) 79–84.
[50] A. Harabi Studies of an alumina–chromia system containing mullite, PhD Thesis, Manchester Materials Science Centre, UMIST, Manchester, 1990.