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Microstructure and related mechanical properties of hot pressed hydroxyapatite ceramics

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Polycrystalline hydroxyapatite (HAP) ceramics were densified by hot pressing. The effects of thermal treatments and of a sintering additive (Na_3PO_4) on the microstructure, flexural strength and fracture toughness were investigated. Hot pressing without additive resulted in dense HAP having a small average grain size (below 0.5 μm). Spontaneous microcracking of the material was also noted. This originated from the thermal expansion anisotropy of HAP crystals. The presence of the sintering aid promotes grain growth. Dense materials exhibited mechanical properties depending on the microstructure. The highest values obtained were 137 MPa and 1.2 $\mathrm{MPa}\sqrt{\mathrm{m}}$ for the flexural strength and fracture toughness, respectively. A decrease of both strength and toughness was observed with increasing average grain size. This behaviour is attributed to the weakening of the grain boundaries by either the development of initial microcracking or the Na_3PO_4 addition. It is concluded that hot pressing is very useful to elaborate dense HAP having good mechanical characteristics.

1. Introduction

Dense polycrystalline hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$:HAP), due to its biocompatibility, has proved to be an attractive material for biological implants [1–3]. However, the investigations devoted to the evaluation of its mechanical properties revealed low values of both flexural strength and associated toughness [4–10]. This great brittleness is the main restriction for potential applications since it precludes the use of dense HAP in mechanically stressed regions of the human body. As noticed by several authors [11–13] ceramic–ceramic composites technology to elaborate HAP-based materials seems a promising way to extend the range of its applications.

It is well known that the incorporation of a ceramic reinforcement (i.e. fibres whiskers, platelets or particles) in a ceramic matrix improves the mechanical properties [14]. In return, compared with the monolithic matrix behaviour, the presence of a reinforcement opposes the sintering process [15, 16].

The utilization of techniques such as hot pressing or hot isostatic pressing combined with the formation of a liquid phase appears useful to enhance the densification kinetic and obtain nearly fully dense composites. It is therefore important to understand the behaviour of the monolithic matrix densified with these processing routes prior to composite elaboration. In this field, little attention has been given to HAP until now, though the addition of lithium phosphate (Li_3PO_4) has been investigated [17].

This work consisted in determining the influence of hot pressing and the effect of sodium phosphate (Na_3PO_4) as a sintering aid on the densification, strength, toughness and related microstructure of HAP. The aim of the study was to optimize the mechanical properties of a dense hot-pressed HAP matrix for further composite elaboration.

2. Experimental procedure

A commercial powder (Bioland) was used for the preparation of hydroxyapatite materials. It was calcined at 750 °C and coarsely crushed into small agglomerates. This powder had a stoechiometric ratio Ca/P = 1.67 and a specific surface area, measured by BET (rapid surface area analyzer Micromeritics 2205), of 23.5 $m^2\,g^{-1}$. However, the presence of agglomerates leads to an underestimation of the real value of the specific surface area of the powder. The average particle size was estimated around 45 nm. The pure powder was either sintered in air or hot pressed at various temperatures and holding times under a constant compressive stress of 20 MPa in an argon atmosphere (heating and cooling rate were 15 °C min^{-1} and 10 °C min^{-1}, respectively).

The addition of Na_3PO_4 as sintering aid has also been investigated. This additive was used because of its biocompatibility and its chemical similarity with Li_3PO_4 which was found to enhance the densification process of the HAP [17]. Thus, Na_3PO_4 was also assumed to promote the formation of a liquid phase during sintering. The blended powders, HAP containing up to 5 wt% of Na_3PO_4, 12 H_2O as Na_3PO_4 source, were hot pressed in the same conditions as the pure powder.

Sintered blocks, 30 x 30 x 5 mm, were cut into bars using a diamond saw and each bar was polished with a 3 μm diamond paste. The relative density of the samples was measured by the Archimedean method in dibutylphtalate (theoretical density of HAP was assumed to be 3.156 g cm^{-3}). The average grain size was estimated, from scanning electron microscopy micrographs of chemically etched surfaces (lactic acid 0.15 M), using the linear intercept method (AFNOR NF A 04-502).

The flexural strength was determined by three-point bending on 25 x 4 x 4 mm bars with a 20 mm span and a crosshead speed of 0.5 mm min^{-1}. The fracture toughness was calculated from the single edge notched bend technique (SENB). For this experiment, the bars were notched to a depth (a) of a quarter of the total height (*h*) of each specimen using a diamond saw. The strength was then measured according to the above mentioned procedure and the toughness calculated from the following equation:

$$K_{1c} = Y\sigma a^{1/2}$$

with

$$Y = 1.96 - 2.75(a/h) + 13.66(a/h)^2 - 23.98(a/h)^3 + 25.22(a/h)^4.$$

For these mechanical characteristics, five samples were tested per result point.

3. Results and discussion

3.1. Microstructure

The relative density and average grain size of pure HAP as a function of hot pressing temperature and duration are presented in Table I. After 30 min at 1100 °C the measured densities were close to the theoretical value. For comparison, the same powder sintered in air at 1100 °C for 5 h and at 1250 °C for 30 min exhibited a final densification rate of 89% and 95.5%, respectively. Thus, the 20 MPa applied stress fairly enhances the densification process of the HAP.

An increase of the average grain size with increasing temperature was also observed. An estimation of the apparent activation energy for grain growth, calculated from the least-squares fit of Lnd_m versus $1/T$, was $E_a = 122 \pm 10$ kJ mol^{-1} (Fig. 1). This value is lower than those found in the literature for sintered HAP (from 140 to 240 kJ mol^{-1}) [4, 7], but it is important to note that these energies do not have to be associated with the real activation energy of the diffusional mechanism. Indeed, the grain size can be formulated generally by $d = Kt^{1/n}$ (if the initial grain size d_0 is negligible), when n ranges from 2 to 4 and represents the diffusional process. The real value of the activation energy which corresponds to the diffusional process would be $E'_a = nE_a$ [18]. In our experiment d_0 was neglected (in any case $d^n > 10d^n_o$, except for the first point at 1000 °C).

TABLE I Relative density and average grain size of hot pressed HAP

T(°C)	t(min)	D(% dth)	d_m(μm)
900	30	54	–
1000	30	87.1	0.10
1040	30	93	0.15
1100	30	98.8	0.20
1150	30	99	0.35
1200	30	99.5	0.40
1250	30	99.2	0.75
1250	60	99	0.80
1250	600	98.8	1.20

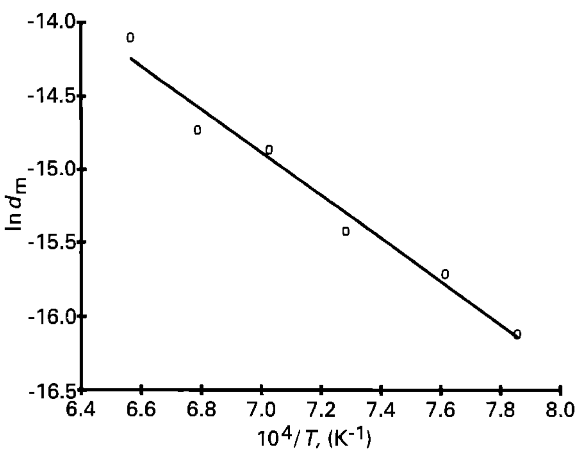

Figure 1 Ln d_m versus reciprocal temperature for 30 min–20 MPa hot pressed HAP.

The reduction of the densification temperature and duration induced by the applied stress resulted in dense HAP with an average grain size below 0.5 μm whereas natural sintering hardly leads to grains smaller than 3 μm [6–8]. So, hot pressing appears helpful in the elaboration of HAP materials with a fine microstructure. Similar results were pointed out by Hirayama *et al.* [9] for hot isostatic pressed HAP.

A typical microstructure of dense hot pressed HAP is shown in Fig. 2. On the fracture surface (Fig. 2b) numerous microcracks perpendicular to the fracture plane were observed. From a theoretical point of view [19–21], the microcracking can be due to the thermal expansion anisotropy (TEA) of the lattice of non-cubic crystals structure. During cooling, this TEA induces the development of residual stresses at the grain boundaries between grains of different orientation. The local stress intensity, which depends on both the difference between the linear coefficients of thermal expansion of the lattice and the grain size, may provoke microcracking.

In the same way, the combination of the two following factors can be taken into account to explain the observed microcracking in dense hot pressed HAP:

1. A great thermal expansion anisotropy of the hexagonal lattice of the hydroxyapatite. According to Fischer *et al.* [22], the linear coefficients of thermal expansion would be about 13×10^{-6} K^{-1} and 22×10^{-6} K^{-1} (average values in the 0–1000 °C temperature range) for the directions a and c of the lattice respectively, that is to say a difference $\Delta\alpha$ close to 10×10^{-6}K^{-1}.

2. The low fracture toughness and strength of the material, as exposed hereafter. A microcracking initiated by a too high cooling rate can be excluded.

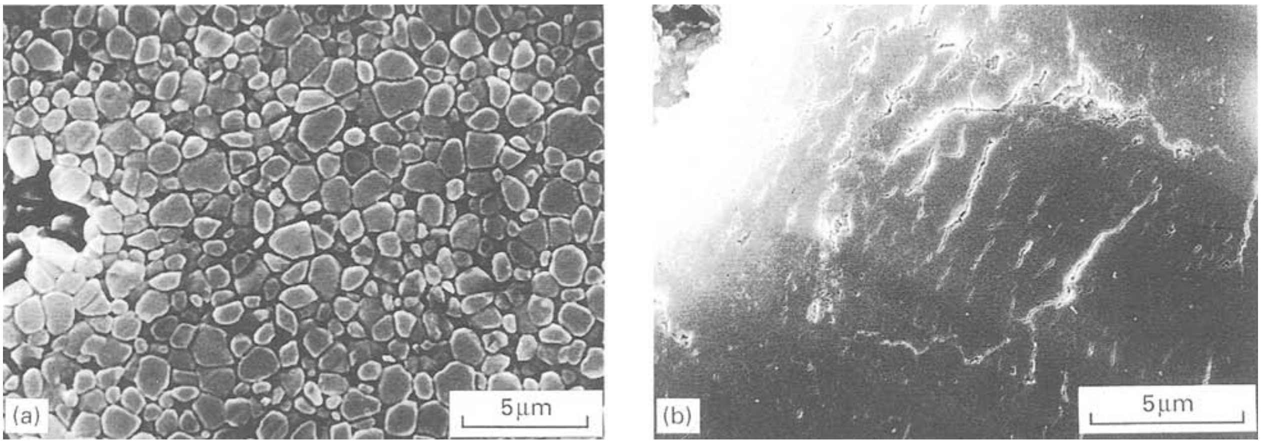

Figure 2 SEM (a) etched surface of HAP (1250 °C–600 min–20 MPa); (b) fracture surface of HAP (1200 °C–30 min–20 MPa); smooth region of transgranular failure.

TABLE II Influence of Na_3PO_4 on the measured characteristics of hot pressed HAP

HP (20 MPa)	1000 °C–30 min	1200 °C–30 min		
Na_3PO_4,12H_2O (wt %)	2	0.6	2	5
D (%dth)	97.5	99.4	99.6	99.5
d_m (μm)	0.30	0.40	1.10	1.25
σ_f (MPa)	74 ± 3	95 ± 10	82 ± 6	78 ± 7
K_{1C} (MPa $\sqrt{m}$)	-	0.97 ± 0.05	0.96 ± 0.05	0.94 ± 0.05

Indeed, if we consider the first parameter of thermal shock resistance, which represents the instantaneous temperature difference required to induce a microcrack [23]:

$$R = \sigma_f(1 - \nu)/\alpha E$$

with the assumption that for a dense HAP Poisson's ratio is inferior to 0.3 and Young's modulus below 100 GPa [6–8], a minimum value for R would be around 40 °C (with $\sigma_f = 130$ MPa and $\alpha = 22 \times 10^{-6}$ K^{-1}). Thus, the effect of the cooling rate (10 °C min^{-1}) on the initiation of microcracks can be neglected.

The results obtained for hot pressed HAP containing various amounts of sintering aid are summarized in Table II. The addition of Na_3PO_4 did not seem to modify the HAP phase and no evidence for any other crystalline phase was detected on the X-ray diffraction patterns of the different materials.

Hot pressing performed at 1200 °C–30 min–20 MPa, which in any case leads to dense materials, showed that the presence of Na_3PO_4 had induced significant grain growth. Indeed, the average grain size of a 5 wt % added HAP was of the same order of magnitude (about 1.2 μm) after 30 min as the one obtained with pure HAP after 10 h at 1200 °C (under 20 MPa).

Samples containing 0.95 wt % Na_3PO_4 (with respect to the 2 wt % of initial hydrate) and pressed at 1000 °C for 30 min were 97.5% dense. In comparison with the values achieved for hot pressed HAP without additive, this result corresponds to a decrease of about 50 °C in the densification temperature. This proves the efficiency of Na_3PO_4 as a hydroxyapatite sintering aid, even at a low content.

3.2. Strength and toughness

Flexural strength σ_f and fracture toughness K_{1C} versus average grain size of pure hot pressed HAP are plotted on Figs 3 and 4. Evidence exists for similar variations of these two characteristics and both curves can be divided into two distinct domains. In the first one, for grains smaller than 0.4 μm, the mechanical characteristics increased with increasing grain size up to 137 ± 5 MPa for the flexural strength and 1.20 ± 0.05 MPa $\sqrt{m}$ for the fracture toughness. These data correspond to an average grain size of 0.4 μm associated with the highest final density (99.5% of theoretical density). In fact, for these small grain sizes, the evolution of the mechanical properties must be related to the relative density rather than to the grain size of the material (Fig. 3). Indeed, for porous ceramic materials, strength data classically agree with the expression $\sigma_f = \sigma_0 \exp(-bP)$, in which P designates the residual porosity (in our experiment $\sigma_o = 140$ MPa and $b = 7$). Thus, it is the residual porosity which governs the fracture strength and constitutes the source of critical defects for failure, accounting for similar variations of strength and toughness.

In the second domain, for $d_m \geqslant 0.4$ μm, that is to say for dense materials, the mechanical characteristics decreased with increasing average grain size. SEM examination of the fracture surfaces (Fig. 5) revealed changes in the crack propagation between the different materials. The fracture surface (Fig. 5a) of a

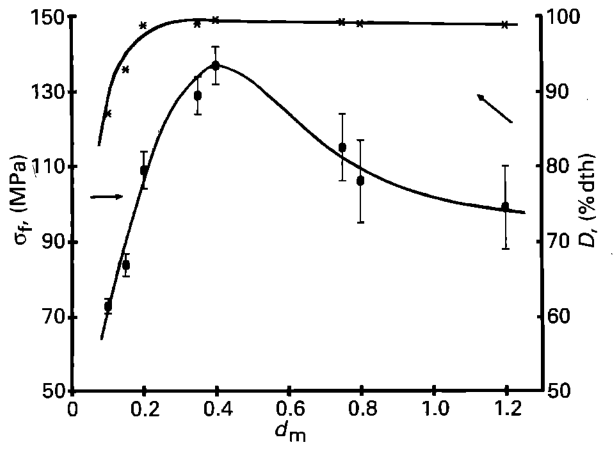

Figure 3 Fracture strength and relative density of pure hot pressed HAP versus average grain size.

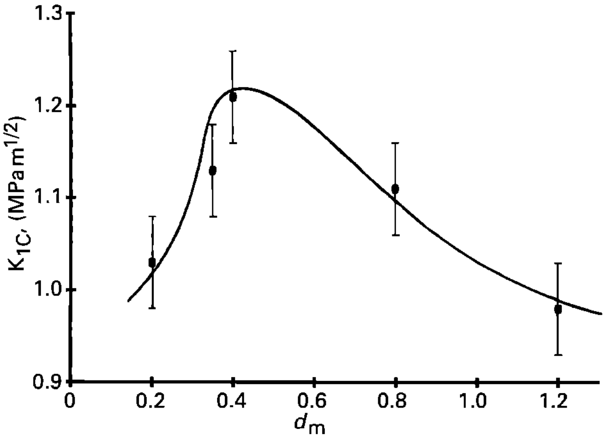

Figure 4 Fracture toughness of pure hot pressed HAP versus average grain size.

1200 °C–30 min–20 MPa hot pressed HAP, which exhibited the highest mechanical properties, showed that the crack had essentially propagated between agglomerates. This behaviour produced important crack deflections and resulted in a very rough surface. To a lesser extent some smooth regions, commonly known as fracture mirrors, were also observed, indicating that some agglomerates had been broken (Fig. 2b). In these zones the propagation could be ranked as a transgranular mode of failure. In contrast, the fracture surface of a 1250 °C–10 h–20 MPa hot pressed HAP material, associated with the greatest average grain size (1.2 μm) and lowest mechanical properties, was perceptibly different. The surface was smoother and the crack seemed to have propagated on an intergranular mode of failure, resulting in fewer deflections (Fig. 5b).

From these microstructural observations, the following hypothesis can be put forward to understand the mechanical behaviour of these dense HAP materials. The decrease of the flexural strength would seem to result from the development of the initial microcracking associated with grain growth, as discussed in the previous section. The extension of the microcracks along grain boundaries weakens the material and consequently promotes the decrease of rupture resistance. The appearance of easy paths in the main crack plane, which accompanies this phenomenon, also leads to the reduction of crack deflections. This accounts for the change in failure mode, from interagglomerates in the case of fine grains HAP (0.4 μm) to intergranular for coarser grain materials (1.2 μm), and for the softening effect observed on fracture surface roughness. Assuming that crack deflection is recognized to be an efficient reinforcement mechanism [24] (noticeably studied and researched in composite materials [25]), the decrease in fracture toughness would seem to originate from the decrease in crack deflection during the failure process.

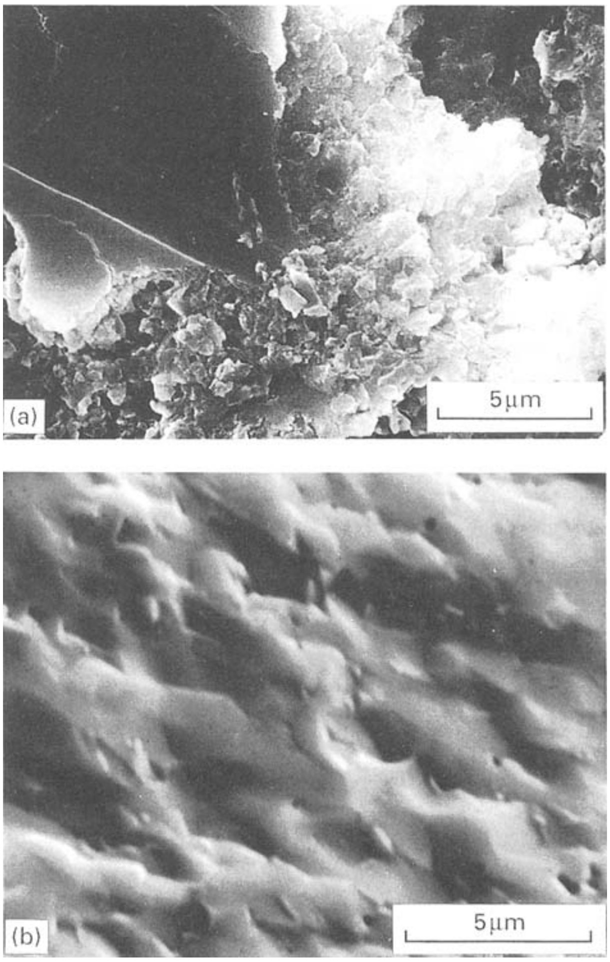

Figure 5 SEM fracture sufaces (a) 1200 °C–30 min–20 MPa; (b) 1250 °C–10 h–20 MPa

It is worth noting that for a dense HAP having a small grain size (0.4 μm), the microcracks do not seem detrimental to the mechanical resistance. Indeed, they appear perpendicular to the crack propagation plane (Fig. 2b). However, they do not lead to any toughening of the material either, since no crack branching, associated with the reinforcement mechanism by microcracking [19, 22], was observed on fracture surfaces.

The mechanical characteristics of hot pressed HAP with various amounts of Na_3PO_4 addition are given in Table II. Compared with pure hot pressed HAP powder, the presence of the sintering aid increased the brittleness of the material. But, in contrast even if the flexural strength of dense HAP (hot pressing at 1200 °C–30 min–20 MPa) decreased with increasing Na_3PO_4 amount or average grain size, the fracture toughness remained constant ($K_{1C} = 0.95$ MPa$\sqrt{m}$).

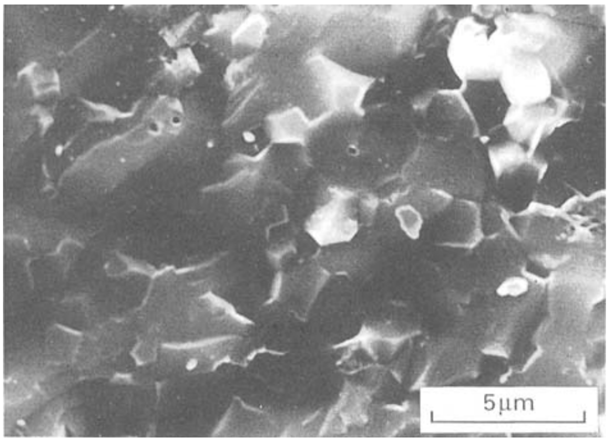

Figure 6 SEM fracture surface of a 5 wt % added HAP (1200 °C–30 min–20 MPa).

The examination of fracture surfaces (Fig. 6) revealed typical intergranular mode of rupture, grain facets being clearly observed. Moreover, the K_{1C} value corresponds to the one determined on pure HAP with a 1.2 µm grain size, for which intergranular mode of failure was also observed. Thus, whether or not the microcracking development can account for the decrease in toughness of pure HAP, the presence of the sintering aid appears to be the limiting parameter for the fracture toughness of added HAP, the grain size having no influence on this characteristic. The slight decrease in the flexural strength could, in the same way, be attributed to a weakening of the grain boundaries resistance due to the Na_3PO_4 addition.

From the compared results it might be hypothesized that Na_3PO_4 would facilitate the accommodation of thermal expansion anisotropy and limit microcracking through the formation of a liquid phase and glassy intergranular films. However, this hypothesis has not been confirmed because of the difficulty encountered in revealing the microcracks, which can only be seen when perpendicular to the rupture plane on a mirror area (i.e. on the regions of transgranular failure).

4. Conclusion

This study allowed us to point out the important effects of microstructure on the mechanical behaviour of dense polycrystalline HAP materials. Spontaneous microcracking attributed to thermal expansion anisotropy of hydroxyapatite crystals was observed. This phenomenon can be considered as a major parameter limiting the mechanical properties.

The applied stress allows us to decrease the temperature and duration required to densify the HAP, which consequently prevents grain growth. From this point of view, the elaboration of dense HAP by hot pressing appears useful in decreasing the microcracking during cooling. Thus, hot pressing minimizes these two detrimental parameters, temperature and grain size, on the microcracking phenomenon.

The addition of Na_3PO_4 as sintering aid to enhance the densification rate is favourable to further decrease the sintering temperature but in return, induces much more grain growth and weakens the grain boundaries which finally results in lower mechanical characteristics.

It is also interesting to note that the highest values of the flexural strength (137 MPa) and toughness (1.2 MPa $\sqrt{m}$) obtained for a dense HAP having small grains ($d_m = 0.4$ µm) are slightly superior to the literature data for natural sintered HAP [4–8] which are generally densified at higher temperature and longer holding time (it must be kept in mind that the measured strength and toughness values depend upon the specimen geometry and polishing as well as testing parameters).

On the contrary, this strength remains lower than the values given by Hirayama [9] for HIPed HAP at very low temperature, resulting in 0.3 µm average grain size materials presenting strength over 200 MPa. Nevertheless, the fracture toughness was not increased compared with the present study. To conclude, it seems clear that the elaboration of dense HAP materials with optimized mechanical properties requires minimization of the thermal expansion anisotropy and grain growth.

If hot pressing or hot isostatic pressing can be used successfully to enhance the fracture strength of HAP, a subsequent increase in the fracture toughness seems hardly directly feasible. To this end, composite technology to toughen the material appears necessary.

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