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Characterization of hot pressed Al_2O_3-platelet reinforced hydroxyapatite composites

E. CHAMPION, S. GAUTIER, D. BERNACHE-ASSOLLANT
Laboratoire de Matériaux Céramiques et Traitements de Surface, URA CNRS 320, 123, avenue Albert Thomas, 87060 Limoges – France

Hydroxyapatite reinforced with monocrystalline Al_2O_3 platelets was densified by hot pressing. The effect of volume fraction and size of platelets on the microstructure, strength and toughness was investigated. It was demonstrated that no phase degradation occured during thermal treatments. A better homogeneity of composite mixtures was achieved when large platelets had been used. In return, the incorporation of small platelets appeared more favourable to increase the mechanical characteristics although limiting effect induced by microstructural defects. The flexural strength can reach 140 MPa with an associated fracture toughness of 2.5 MPa $\sqrt{m}$ compared to 137 MPa and 1.2 MPa $\sqrt{m}$ for dense monolithic HAP. The observation of crack propagation allowed us to point out the mechanisms responsible of this toughening. Crack deflection on disk faces should be considered as the initiating phenomenon leading to platelet debonding, crack bridging or branching. Crack deflection and branching may also result in the formation of unbroken ligaments of material which bridge the crack.

1. Introduction

Several ceramics, due to their biocompatibility, have become attractive materials for the repair of damaged hard tissues of the human body [1–3]. Among these bioceramics, particular attention has been given to hydroxyapatite (HAP), whose chemical composition $Ca_{10}(PO_4)_6(OH)_2$ is similar to that of the mineral bone. The ability of HAP to form bioactive fixation with the surrounding bone tissues is well known and orthopaedic applications are now under development [4–7]. However, evaluations of mechanical properties of dense HAP show high brittleness with low tensile strength associated with a fracture toughness which hardly exceeds 1 MPA $\sqrt{m}$ [8–15]. As a result, implantation of this material is restricted to unstressed regions of the body and further extensions of its applications require significant improvement of its mechanical characteristics.

As reviewed by R. W. Rice [16], the presence of a ceramic second phase dispersed in a ceramic matrix may induce energy dissipative mechanisms and enhance the mechanical behaviour. The incorporation of tetragonal zirconia particles, successfully used to toughen ceramic matrices by stress-induced transformation and local microcracking [17, 18], seemed the most promising way to reinforce the HAP. However, full stabilization of ZrO_2 particles in the cubic form by calcium diffusion and HAP decomposition into tricalcium phosphate (TCP) after sintering were often reported [19, 20]. This hinders the expected transformation toughening mechanism to develop. Reinforcement by alumina spherical dispersoids was also investigated but similar difficulties were noted with TCP and calcium aluminates formed during sintering [21, 22]. Nevertheless, an increase of the fracture toughness was observed either with ZrO_2 [23, 24] or Al_2O_3 [22, 25] when hot pressing techniques were used to facilitate the densification process of the HAP matrix.

During the past few years, monocrystalline platelets have been studied as a possible alternative to whiskers or particles for composite materials. Indeed, a disc-shaped morphology can be particularly favourable to toughen brittle matrices by crack deflection mechanisms [26–28]. From this assumption, this work consisted in the elaboration of dense HAP–Al_2O_3 platelet composites by hot pressing. The objective was to investigate the strengthening and toughening potentialities induced by the introduction of various volume fractions of platelets having different sizes.

2. Experimental procedures

2.1. Composites preparation

Commercial raw materials were used to elaborate the composites. Hydroxyapatite powder (Bioland) was calcined at 750 °C and ball milled for 2 h in an alumina container in order to break the agglomerates. This powder had a stoichiometric ratio Ca/P = 1.67 and a specific surface area, measured by the BET method (rapid surface analyser Micromeritics 2205) of $30\ m^2\ g^{-1}$. Alumina platelets (Elf Atochem) were monocrystals of α-Al_2O_3 (corundum phase). Two different grades of platelet powders were used; their main characteristics are listed in Table I. T'0 Al_2O_3 was in the form of agglomerates as large as 300 μm (Fig. 1a).

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TABLE I Characteristic of alumina platelets

Grade	Diameter (μm)	Thickness (μm)	Specific area ($m^2 g^{-1}$)	Purity specifications
T'0	3–5	0.3	0.8	α-Al_2O_3 >97.5%
T2	10–15	0.7	1.0	impurities: F, Li, Na

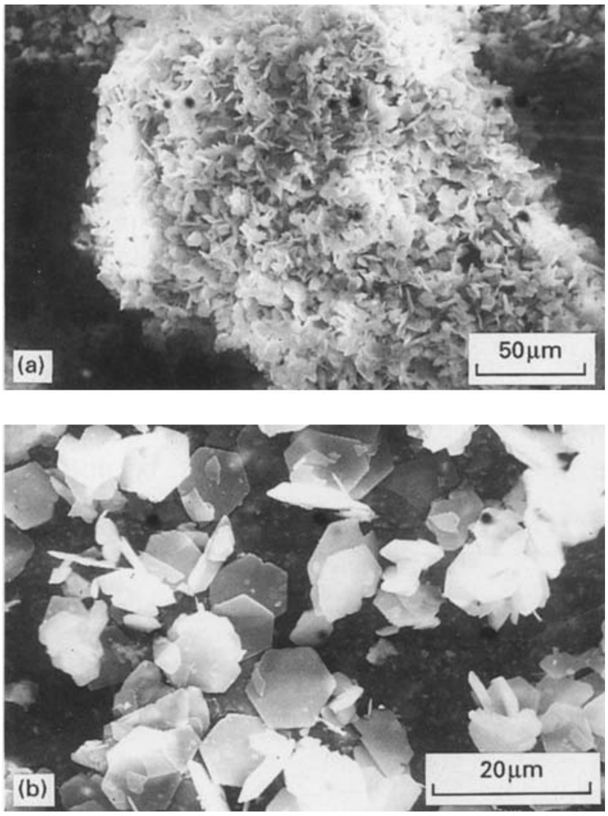


Figure 1 SEM of alumina platelets: (a) agglomerate in grade T'0; (b) grade T2.

T2 grade was less agglomerated but some fragments of broken platelets were observed (Fig. 1b).

Composite mixtures containing 20 vol % and 30 vol % of Al_2O_3 were prepared by homogenizing the blended powders in demineralized water. Green bodies, made by pressure filtering of the slurry, were densified by hot pressing at 1100 °C to 1250 °C temperature under a constant compressive stress of 30 MPa in an argon atmosphere (heating and cooling rate were 20 °C min^{-1}). Thermal treatment parameters were adjusted for each material to obtain comparable and high densification rates whatever the composition. Indeed, the effect of porosity, which is known to significantly diminish the mechanical characteristics of HAP [15], would make it impossible to evaluate the influence of microstructural and morphological parameters associated with the reinforcing phase.

2.2. Sample characterization

Sintered blocks 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 water (theoretical densities of HAP and Al_2O_3 were assumed to be 3.156 g cm^{-3} and 3.98 g cm^{-3}, respectively). The average grain size of the matrix was estimated from scanning electron microscopy (SEM) micrographs of chemically etched surfaces (lactic acid 0.15 M). X-ray diffraction patterns on powdered composites were recorded, with CuK_α radiation on a Philips goniometer, to analyse the phases obtained in the sintered products. The phases were determined from comparison with the JCPDS reference data file.

The flexural strength was determined by three-point bending on 25 × 4 × 4 mm samples with a 20 mm span and a crosshead speed of 0.2 mm min^{-1}. The fracture toughness was calculated from the single edge notched bend technique (SENB). In this experiment, the bars were notched to a depth (a) of a quarter of the total height (h) of each specimen using a 0.3 mm width diamond saw. The strength was then measured, by three-point bending, according to the above mentioned procedure and the toughness calculated from the following equation:

$$K_{1c} = Y \sigma_r \sqrt{a}$$

with

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

For the mechanical characterization, between five and eight samples were tested per result point.

3. Results and discussion

3.1. Microstructure

The different compositions, thermal treatments and relative density measured on sintered samples are summarized in Table II.

Typical XRD patterns of the starting mixtures and hot pressed composites are presented in Figs 2 and 3. It can be seen that neither the sintering temperature (Fig. 2) nor the starting composition (Fig. 3) have an influence on the remaining phases after hot pressing. HAP and α-Al_2O_3 are the main phases contained in the composite materials. There is no evidence of any reaction between Al_2O_3 and HAP during the sintering process since no calcium aluminates or other phases

TABLE II Composition, sintering conditions and relative density of materials

Composition (ref. N°)	Hot pressing	D (%D_{TH})
HAP matrix (0) [15]	1200 °C–30 min–20 MPa	99.5
HAP 20% Al_2O_3 T'0 (1)	1100 °C–2 h–30 MPa	96.4
HAP 20% Al_2O_3 T'0 (2)	1200 °C–2 h–30 MPa	97.0
HAP 20% Al_2O_3 T'0 (3)	1250 °C–2 h–30 MPa	96.5
HAP 30% Al_2O_3 T'0 (4)	1200 °C–2 h–30 MPa	97.0
HAP 30% Al_2O_3 T'0 (5)	1250 °C–2 h–30 MPa	98.0
HAP 20% Al_2O_3 T2 (6)	1200 °C–2 h–30 MPa	98.2
HAP 20% Al_2O_3 T2 (7)	1250 °C–2 h–30 MPa	98.0
HAP 30% Al_2O_3 T2 (8)	1250 °C–2 h–30 MPa	96.2

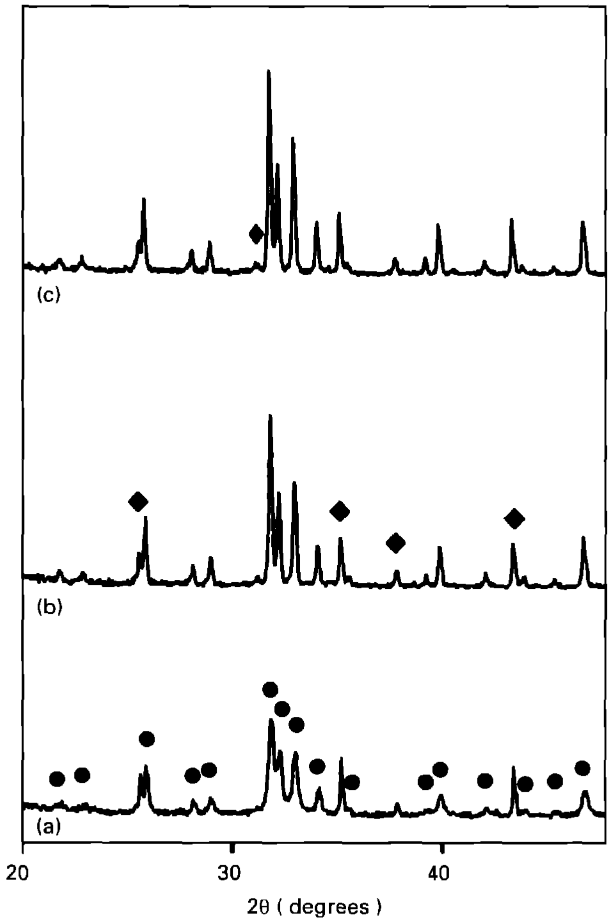


Figure 2 XRD patterns of HAP–20 vol % Al_2O_3 T'0; influence of HP temperature. (a) Green; ● $Ca_{10}(PO_4)_6(OH)_2$ (b) 1100 °C, 2 h; ◆ Al_2O_3 (c) 1250 °C, 2 h; ◆ $Ca_3(PO_4)_2$.

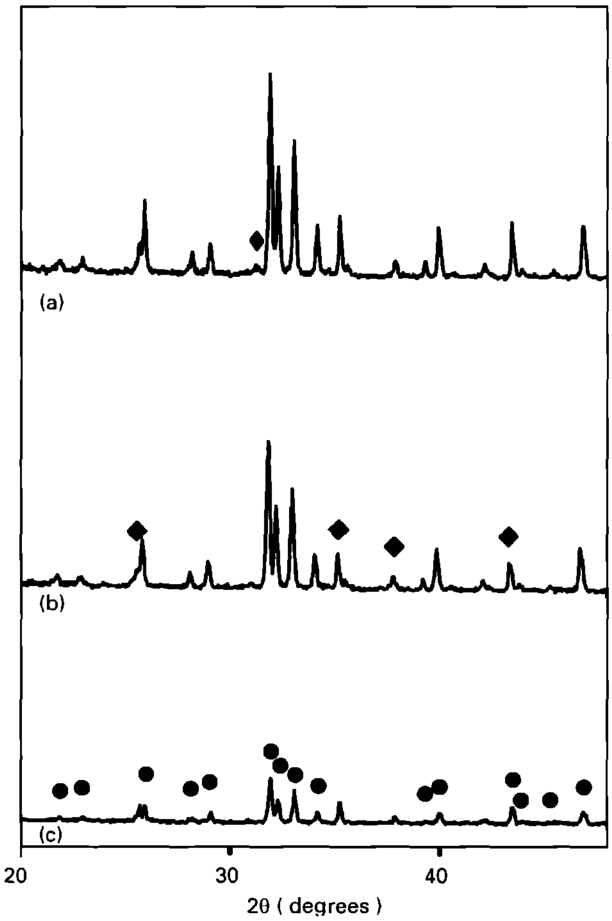


Figure 3 XRD patterns of 1200 °C–2 h–30 MPa HP materials; influence of composite composition: (a) 20 vol % Al_2O_3(T'0), ◆ $Ca_3(PO_4)_2$; (b) 20 vol % Al_2O_3(T2), ◆ Al_2O_3; (c) 30 vol % Al_2O_3(T'0) ● $Ca_{10}(PO_4)_6(OH)_2$.

were detected. Traces of β-TCP were always observed above the 1100 °C thermal treatment. However, the very low intensity of the main diffraction peak for β-TCP ($2\theta = 31°$), even after hot pressing at 1250 °C, indicates that the amount of this phase is not related to the treatment temperature. It should be assumed that β-TCP would be derived from a slightly non-stoichiometric Ca/P ratio of the starting powder rather than from HAP decomposition during sintering. Moreover, this hypothesis is consistent with the latest studies demonstrating that pure HAP does not decompose into calcium phosphates below 1450 °C [29], the presence of TCP at lower temperature being attributed to an atomic ratio Ca/P different from the stoichiometric value of 1.667 [30].

As no significant phase change was noted after sintering, the theoretical densities of the composites were calculated with a simple mixture rule from the starting powders data (i.e. 3.32 g cm^{-3} and 3.40 g cm^{-3} for the 20 vol % and 30 vol % Al_2O_3 composites, respectively). For all the experiments, nearly fully dense composites were obtained. Relative densities of hot pressed materials ranged between 96.2% and 98.2% with a standard deviation of ± 0.6%. The incorporation of inert Al_2O_3 dispersoids opposed the sintering process of the HAP matrix, in agreement with the known theoretical models [31]. In comparison with the monolithic matrix, although hot pressing conditions were more severe, the densification rate of the composites remained inferior. These conditions also led to a significant growth of HAP grains: 0.8 μm, 1.8 μm and 3 μm at 1100 °C, 1200 °C and 1250 °C, respectively, whereas a 20 MPa applied stress at 1200 °C for 30 min resulted in a 0.4 μm average grain size and 1.2 μm after 10 h at 1250 °C for pure hot pressed HAP [15]. "Two hypothesis can be taken into account to explain this important increase of the HAP grain size in composite materials:

(i) the increase of the applied stress during hot pressing, from 20 MPa for pure HAP to 30 MPa for composites,

(ii) the impurities contained in platelet powders (as listed in Table I). Indeed, some lithium, sodium and fluorine based compounds constitute sintering aids to promote HAP densification and consequently may enhance grain growth."

A typical microstructure of the composites is shown in Fig. 4. Evidence exists for preferential orientation of the platelets which tend to lie in planes perpendicular to the direction of the applied stress during hot pressing (arrow on Fig. 4).

Some heterogeneities in platelet distribution within the matrix were also observed, and can be divided into two categories:

(i) Small groups formed by two or three non-individualized platelets, piled on top of each other (Fig. 4).

(ii) Platelet agglomerates with an average size of approximatively 50 μm width and 10 μm thick (Fig. 5). They were formed of muddled up platelets which the

HAP matrix had not penetrated. Thus, they constitute porous regions without strong cohesion.

These microstructural defects result from the difficulty encountered in obtaining homogeneous mixtures of HAP powder and platelets. The two types of defects were present when small platelets (T'0) were used, on account of their strong initial agglomeration. A majority of type (i) defects were noted in T2-containing materials, few porous agglomerates being observed. Thus, good homogeneity of the initial mixtures is a required condition to fully densify the composites since intra-agglomerate porosity cannot be filled by the matrix during the sintering process.

3.2. Strength and toughness

As mentioned previously, the distribution of platelets within the matrix was anisotropic. Thus, composite characteristics depend on the measurement direction.

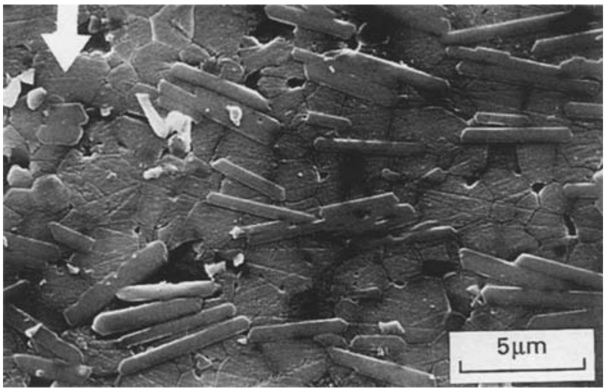


Figure 4 SEM of etched surface (composite N°2) – preferential orientation of platelets.

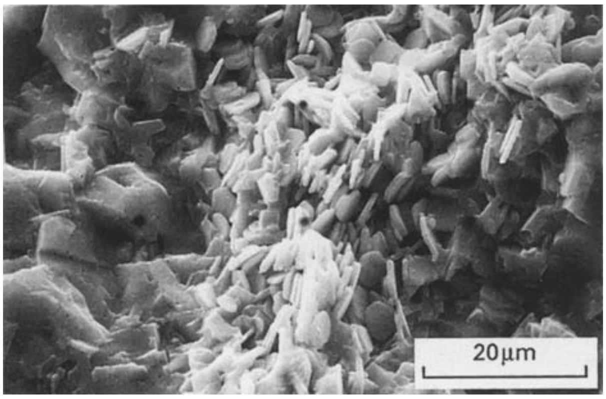


Figure 5 SEM of fracture surface (composite N°2) – agglomerate of T'0 platelets.

For mechanical testing, the stress was applied in the same direction as during hot pressing (see arrow on Fig. 4).

Flexural ultimate strength σ_r and fracture toughness K_{1c} measured on the composites are given in Table III. Compared with the values obtained for dense hot pressed HAP matrix, most of materials exhibited lower strength. Several microstructural parameters can explain this decrease. Residual porosity and grain size, known to most significantly influence the mechanical behaviour of ceramic materials, could provide the first explanations. "From this point of view, the lower densification rate (inferior to 98% against 99.5%) and the greater average grain size of the HAP matrix (over 0.8 µm against 0.4 µm) could explain the decrease of the fracture strength for the composites in comparison with the monolith. Nevertheless, the presence of heterogeneities in platelets repartition prevents a precise evaluation of the reduction in strength which could result from the microstructural parameters as discussed hereafter."

When T'0 Al_2O_3 was used, platelet agglomerates constituted large size defects and can be considered to be the main limiting effect. Thus, for 20 vol % Al_2O_3 [1–3] the flexural strength remained unchanged whatever the densification rate or average grain size. In spite of this, some noticeable tendencies can be pointed out to prove the efficiency of Al_2O_3 platelets to strengthen the HAP. It is interesting to note that agglomerates are regions containing a very high Al_2O_3 volume fraction. This also means that homogeneous dense regions contain a lower fraction of platelets than the total average amount. Thus, apart from the detrimental effect of the agglomerates themselves, only part of the 20 or 30 vol % of the reinforcing phase contributed to the mechanical characteristics. And, even in these conditions, at 30 vol % Al_2O_3–T'0, the flexural strength reached 140 MPa with a fracture toughness of 2.5 MPa $\sqrt{m}$. This result demonstrates that it is possible to preserve good strength while increasing significantly the resistance to crack propagation, even in the presence of microstructural heterogeneities. Therefore it can be thought that the removal of agglomerates should lead to much higher values of both strength and toughness since the effective volume fraction of Al_2O_3 mechanically solicited would be higher (equal to the total added fraction).

With T2 grade, at 20 vol %, composites exhibited slightly higher strength than the corresponding T'0 materials. Although giving better homogeneity of the mixtures, the values remained low. Moreover, increasing the volume fraction to 30% led only to 110 MPa

TABLE III Flexural strength and fracture toughness of materials (as referred in Table II)

Parameter	Sample reference number								
	(0)	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
σ_r (MPa)	137 ± 5	95 ± 10	95 ± 10	90 ± 10	110 ± 5	140 ± 20	80 ± 10	108 ± 10	100 ± 20
K_{1c} (MPa $m^{1/2}$)	1.2 ± 0.05	2.0 ± 0.1	2.0 ± 0.2	2.0 ± 0.3	2.0 ± 0.1	2.5 ± 0.1	2.1 ± 0.1	–	2.4 ± 0.1

and 2.4 MPa$\sqrt{m}$. The improvement was noticeably inferior to that obtained with the small platelets. Too large a size of the reinforcing phase could explain this limitation.

As mentioned in Table III, fracture toughness of composites was always significantly higher than the value registered for the dense monolithic matrix. The relative gain was around 65% and exceeded 100% with 30 vol % Al_2O_3, proving the efficiency of platelets to toughen HAP. SEM examination of crack profiles (Figs 6–9) and fracture surfaces (Fig. 10) illustrate the energy dissipative mechanisms induced during crack propagation. Crack deflection, crack bridging or branching and platelet bebonding were also observed. Crack deflection along platelets faces (Figs 6 and 7) was always noted and should be considered as the initiating phenomenon for the other mechanisms to develop. Debonding, particularly visible on fracture surfaces (Fig. 10) occured preferentially when the crack plane was nearly perpendicular to the platelet faces. Crack bridging appeared to be sometimes associated with branching (Figs 7 and 8). The combination of these last two mechanisms could lead to the formation of large unbroken ligaments of material which bridged the main crack (Fig. 9). Therefore, the effect of platelets on the increase of resistance to crack propagation might be seen through a synergy resulting from the interaction and combination of several elementary mechanisms. The individual contribution of each one of them in the toughness increment measured on the composites remains impossible to determine. Nevertheless, the observed mechanisms were consistent with a weak interfacial bond between Al_2O_3 platelets and HAP grains. This hypothesis can be confirmed since no broken platelets were observed in the crack plane. Furthermore, the great difference in thermal expansion coefficients between HAP and Al_2O_3 (average values $15 \times 10^{-6}\,K^{-1}$ and $8 \times 10^{-6}\,K^{-1}$, respectively) should induce residual shear stress at the HAP–Al_2O_3 interface during cooling, favourable to its weakening.

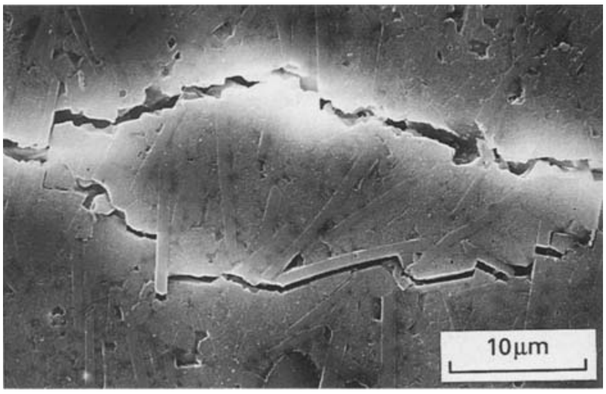


Figure 6 SEM - typical aspect of crack propagation (composite N°6).

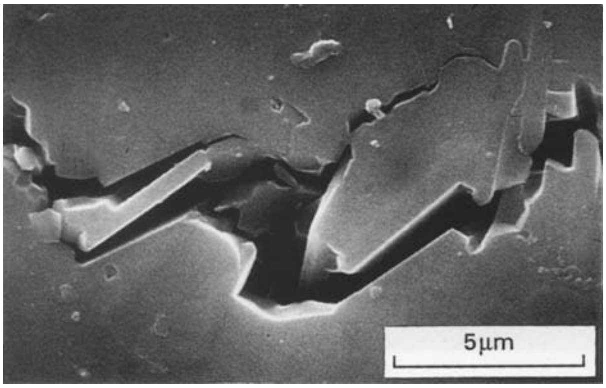


Figure 7 SEM of crack profile (composite N°2) – crack branching and bridging.

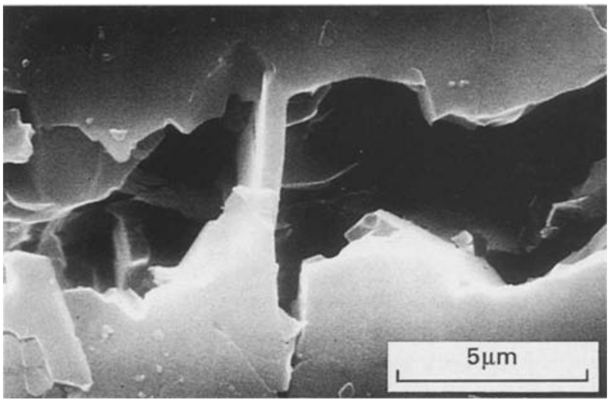
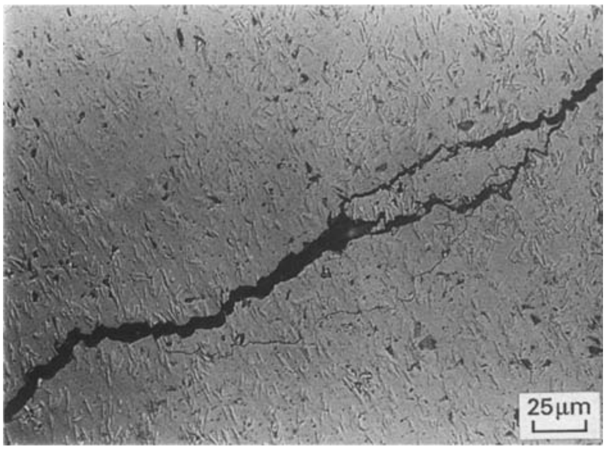


Figure 8 SEM of crack profile (composite N°2) – platelet bridging.



(*Figure 9* SEM of crack profile (composite N°2) – crack branching at macroscopic scale.

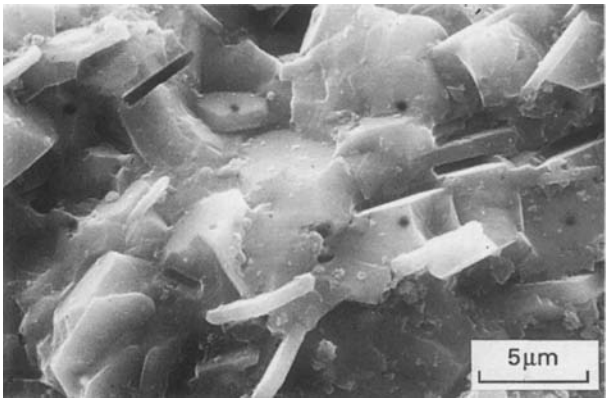


Figure 10 SEM of fracture surface (composite N°2) – platelet bebondings.

4. Conclusions

This study allowed us to establish the real efficiency of Al_2O_3 disc-shaped inclusions in improving the mechanical reliability of HAP. To this end, the use of hot pressing to densify the composite material appeared very helpful since it permits a high densification rate without degradation of the initial phases. The toughening should be assumed to result from the presence of a weak interface between HAP and Al_2O_3. The energy dissipative mechanisms are based on initial crack deflection on Al_2O_3 disc faces followed by platelet debonding, crack bridging and branching. It is important to note that the highest value of toughness measured on composites (2.5 MPa $\sqrt{m}$) is slightly higher than the literature data where spherical particles were used (no study being actually available concerning disc-shaped reinforcement) [22, 25]. It is also interesting to compare our results with the mechanical characteristics of human cortical bone. According to several authors [32, 33], tensile or bending strength (measured on femur or tibia) ranks between 120 MPa and 180 MPa, fracture toughness being found to decrease from 4.5 MPa $\sqrt{m}$ to 2 MPa $\sqrt{m}$ as a function of age. Thus, evidence exists for interesting behaviour of the composites. Moreover, it can be assumed that further improvements of the mechanical characteristics of composites should be obtained, providing better control of the microstructural design. Finally, from a mechanical point of view, reinforcing dense HAP with Al_2O_3 platelets seems to be a promising way to extend its potential applications in orthopaedics.

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