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Processing, Microstructure and Toughness of Al_2O_3 Platelet-Reinforced Hydroxyapatite

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Abstract

Experimental design has been used to analyse the processing of alumina platelet-reinforced hydroxyapatite ceramics. Composite materials were developed by slip casting and hot pressing. The most appropriate slurry composition allowing production of homogeneous composites was 65 wt% of powder and 3·1 wt% of deflocculant. HAP slurries containing up to 20 vol% of platelets had a quasi-Newtonian behaviour and a shear thinning flow was found at 30 vol% of alumina. A preferred orientation of platelets within the matrix was observed which led to anisotropic mechanical characteristics. Platelet incorporation induced strong toughening of the matrix. In comparison with the monolithic HAP ($K_{IC\perp}$ = 0·75 (± 0·15) MPa √m; $K_{IC//}$ = 0·65 (± 0·20) MPa √m), the toughness increased up to 20 vol% of alumina content and reached maximum values of $K_{IC\perp}$ = 2·95 (± 0·45) MPa √m and $K_{IC//}$ = 1·95 (± 0·35) MPa √m. © 1997 Elsevier Science Limited.

1 Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$:HAP), because of its chemical composition close to that of the mineral bone, has biological properties of great interest for osteo-implantation.[1–6] However, HAP ceramics exhibit a very low fracture toughness (about 1 MPa √m)[7–14] which restricts the use to unstressed regions of the body. As reviewed by R. W. Rice,[15] the incorporation of a ceramic second phase dispersed in a ceramic matrix is known to improve the mechanical properties. In this field, some authors have studied alumina reinforcement of HAP and have demonstrated that alumina particles could be efficient for toughening; values of 2 MPa √m were achieved for 20–30 vol% of alumina content.[16,17] Nevertheless, a degradation of HAP and alumina phases with the formation of tricalcium phosphate and calcium aluminates during sintering was also noted.[17,18] In a recent paper,[19] we have shown that alumina platelets could be an attractive alternative to particles. Indeed, in comparison, their incorporation led to a slightly higher toughness (2·5 MPa √m) without phase degradation. As indicated in theoretical analyses,[20,21] disc-shaped inclusions induced energy-dissipative mechanisms based on crack deflection, platelet debonding and crack bridging which generally do not occur in the case of inert spheroïds. Nevertheless, the processing route led to the formation of platelet clusters or aggregates in the materials. Such flaws, also mentioned in the literature for other composite systems containing platelets,[22–24] constitute critical defects which limit mechanical properties. To overcome this problem, it was thought that slip casting of composite slurries could be an appropriate method. Furthermore, this technique should promote a preferred orientation of platelets, lying in parallel planes, more favourable in preventing cluster formation.[25–27] However, if this process appears useful to improve the mechanical reliability, particular attention must be paid to the development of the slurries in order to obtain a high degree of dispersion of the platelets without fracturing them during mixing. Thus, an optimisation of the production conditions is required.

On this basis, our work is concerned with the use of an experimental design to optimise the shaping process of alumina-platelet-reinforced hydroxyapatite. It consisted in investigating the effect of slurry characteristics on slip casting, microstructure and resulting toughness of hot-pressed composites.

2 Experimental Procedure

2.1 Composite preparation

Hydroxyapatite used in this study was a commercial powder (Bioland) calcined at 750°C in air atmosphere. This powder had a stoichiometric ratio Ca/P = 1·667 and a specific surface area of 25 m^2 g^{-1} measured by the BET method (rapid surface analyser, Micrometrics 2205).

Alumina platelets (Elf Atochem, grade T'0) were monocrystals of corundum phase (α-Al_2O_3). Supplier specification gave a purity of 98% of alumina with fluorine as the main impurity. These platelets were characterised by an average thickness of 0·7 μm and a diameter of about 5 μm. This powder had a specific surface area of 0·8 m^2 g^{-1} and was in the form of large platelet agglomerates (about 300 μm).

Composite mixtures, containing up to 30 vol% of alumina platelets, were homogenised in demineralised water and ammonium polymethacrylate as deflocculant, and ball milled in an alumina container. Green compacts were produced by slip casting of the slurries in plaster moulds and were dried for 24 h at 40°C. Then, the densification of the materials was performed by hot pressing at 1200°C for 30 min, under a compressive stress of 30 MPa in an argon atmosphere. The heating and cooling rates were 20°C min^{-1} and 10°C min^{-1}, respectively. These thermal treatment parameters were chosen to obtain nearly fully densified composites, as already reported.[19]

2.2 Characterisation

The rheology of Al_2O_3-HAP slurries was characterised at a constant temperature of 25°C using a rotational viscosimeter (Haake Rotovisco RV20). The relative viscosity of the suspensions was determined at a constant shear rate of 350 s^{-1} applied for 2 min. The rheological behaviour was obtained from the measurement of shear stress versus shear rate. The shear rate was linearly increased up to 450 s^{-1} in 2 min and then decreased down to 0 s^{-1} for the same duration.

The green density of cast mixtures was calculated by geometrical measurements. The relative density of hot pressed samples was measured by the Archimedean method in water. Theoretical densities of HAP-Al_2O_3 composites were calculated from a simple mixture rule of the starting powder data (HAP and Al_2O_3 theoretical densities were assumed to be 3·156 g cm^{-3} and 3·98 g cm^{-3}, respectively).

Scanning electron microscopy (SEM) on chemically etched surfaces (lactic acid 0·15 M) was used for microstructural observations.

Fracture toughness of the materials was estimated by Vickers indentation (durometer Zwick 3212) from the measurement of the lengths of indent radius and cracks. Samples were mirror polished and a 5 N or 54 N indentation load was used for monolithic HAP or composite materials, respectively. K_c values were calculated according to the equation proposed by Evans and Charles:[28,29]

$$\frac{K_c \times \Phi}{H_v \times \sqrt{a}} = 0{\cdot}15 \times k \times \left(\frac{c}{a}\right)^{-3/2}$$

In this equation, fracture toughness, indent radius, crack length and Vickers hardness are designated as K_c, a, c, H_v, respectively. The expression of Vickers hardness and the values of the constants (Φ = 2·7, k = 3·2) allows rewriting the previous relationship as follows:

$$K_c = 0{\cdot}0824 \times \frac{P}{c^{3/2}}$$

For this characterisation, height measurements were made for each result point.

2.3 Experimental analysis

Experimental designs are often used in industry to establish empirical relationships between a measured response and variables.[30] This part of the paper is devoted to the construction and statistical analysis of a two-variable design used to characterise the influence of slurry parameters on composite microstructure. For this experiment, powder (HAP containing 20 vol% Al_2O_3) and deflocculant contents of the slurries have been chosen as the two independent variables, designated as P (%) and D (%), respectively.

The range of investigations was fixed from 50 to 70 wt% for the powder content. Below 50 wt% the quantity of water was too high for slip casting and above 70 wt% the suspensions were too viscous to be cast. The deflocculant content ranged from 3 to 5 wt%, value calculated in reference to the total weight of the slurry (powder plus water).

For the experimental analysis, the ranges of each variable coordinates were reduced between −1 (low level) and +1 (high level) from the real values with the following equations:

$$P_{\text{reduced}} = \left(\frac{P\%_{\text{real}} - 60}{10}\right) \text{ and } D_{\text{reduced}} = \left(\frac{D\%_{\text{real}} - 4}{1}\right)$$

The experiments were uniformly spaced on a two-dimensional surface area (Fig. 1) whose notations and corresponding values of the variables are given in Table 1.

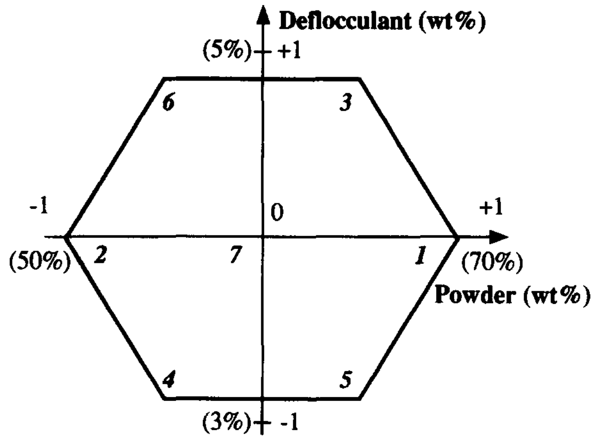

Fig. 1. Schematic representation of experimental design.

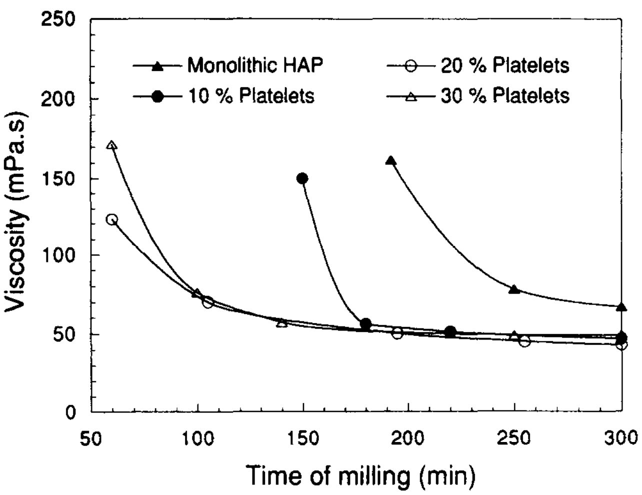

Fig. 2. Relative viscosity of slurries versus ball milling time.

This experimental design was treated using a commercial software (Nemrod 3·0). An empirical relationship $Y_{cal} = f(P,D)$ was calculated to estimate a measured characteristic Y_{exp}, where Y_{cal} can represent either a direct or a simple transformed value of the measured one. According to the number of experiments, the computed equation was given in a polynomial form defined as follows:

$$Y_{cal} = A_0 + A_1P + A_2D + A_3P^2 + A_4D^2 + A_5P \times D$$

The statistical analyses of the computed equation were performed using F-test and Student's test to evaluate the validity of the relationship and the confidence level of its coefficients A_i. When a low confidence level was found the corresponding coefficient was suppressed from the equation and statistical analyses recalculated from the new function.

For the presentation of the results, reduced coordinates ($P \in [-1, +1]$; $D \in [-1, +1]$) were used in the establishment of model equations and real ones ($P\% \in [50, 70]$; $D\% \in [3, 5]$) for graphs.

3 Results and Discussion

3.1 Rheology of suspensions

The different slurries produced in this part were composed of 65 wt% of powder mixture (containing 0, 10, 20 or 30 vol% of Al_2O_3) and 3·13 wt% of deflocculant. This composition has been chosen according to the results obtained in a study of HAP suspensions for slip casting.[31]

The relative viscosity of the slurries versus ball milling time is given in Fig. 2.

For composite suspensions, the relative viscosity of the slurries decreased to reach a constant value of 46 (± 3) mPa s from less than 200 min mixing whereas in the case of pure HAP, the suspension became stable at 67 mPa s only after 280 min. Thus, the incorporation of alumina platelets allowed acceleration of the stabilisation and a lower final viscosity. These results can be explained by both the difference of specific surface area between HAP and Al_2O_3 powders and the disc-shaped morphology of the corundum phase, in agreement with the known analyses.[32–34] Indeed, the total weight content of the slurries being constant, the partial substitution of HAP by Al_2O_3 in the mixtures decreases the concentration of particles and consequently their interactions. Platelet orientation under shear stress can also contribute to the diminution of the relative viscosity. This can be confirmed by the analysis of the rheological behaviour of stable slurries obtained after 5 h milling.

Table 1. Coordinates of experimental design points

N°	*Reduced coordinates*		*Real coordinates*	
	Powder content	*Deflocculant content*	*Powder content (wt%)*	*Deflocculant content (wt%)*
1	+1	0	70	4
2	-1	0	50	4
3	+0·5	+0·866	65	4·866
4	-0·5	-0·866	55	3·134
5	+0·5	-0·866	65	3·134
6	-0·5	+0·866	55	4·866
7	0	0	60	4

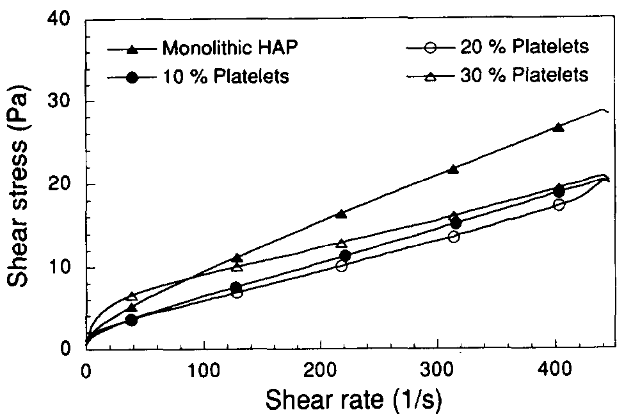

Fig. 3. Rheological behaviour of slurries after 5 h milling.

The curves representing shear stress versus shear rate (Fig. 3) can be divided into two stages. From 50 s^{-1}, the behaviour was linear whatever the composition. For composite mixtures, values of shear stress were lower than that of pure HAP, independently of alumina content. At lower shear rates ($\dot{\gamma}$ <50 s^{-1}) the behaviour of the slurries remained quasi-Newtonian, except in the case of 30 vol% Al_2O_3 content where it was shear thinning. In this region, 30 vol% of Al_2O_3 led to a much higher shear stress which means that there were more interactions between platelets in comparison with 10 or 20 vol% of Al_2O_3. This difference diminished as the shear rate was increased, indicating an orientation of the platelets in the direction of flowing.

Finally, it appears that the incorporation of alumina platelets modifies the characteristics of HAP slurries. In any case, the presence of alumina allows a decrease of the relative viscosity. Up to 20 vol% of Al_2O_3, the slurry exhibits a quasi-Newtonian behaviour while for 30 vol% of Al_2O_3 it becomes pseudoplastic. As indicated by some authors,[23,35] it could be assessed that at high volume content a percolation threshold of the platelets would be reached, requiring a more elevated shear rate to be suppressed by preferred orientation.

3.2 Influence of slurry characteristics

We have shown that it was possible to produce stable composite slurries. However, it was also important to determine their more desirable properties for slip casting. To this end, the experimental design was applied to investigate the influence of deflocculant and total powder content on the relative viscosity of the suspensions, the green density of the cast samples and the final microstructure of hot pressed composites.

Experiments were carried out using a 20 vol% Al_2O_3–80 vol% HAP mixture ball milled for 5 h. The measured viscosity of the slurries (η), relative densities of cast (τ_g) and hot pressed (τ_{hp}) samples are summarised in Table 2.

The treatment of the experimental design data allowed computation of the following empirical equations to transcribe the development of relative viscosity, green density and sintered density versus powder and deflocculant content of the slurry (expressed in the reduced coordinates system):

$$\mathrm{Ln}(\eta) = 3{\cdot}4335 + 0{\cdot}5202 \times P + 0{\cdot}2363 \times P^2 - 0{\cdot}096 \times D^2 \quad (1)$$

$$\tau_g = 49{\cdot}9 - 4{\cdot}4 \times P^2 + 1{\cdot}7333 \times D^2 \quad (2)$$

$$\tau_{hp} = 98{\cdot}95 + 4{\cdot}25 \times P - 4{\cdot}5 \times P^2 - 2{\cdot}223 \times D - 4{\cdot}467 \times D^2 + 6{\cdot}524 \times P \times D \quad (3)$$

Statistical analyses and graphs associated with these relationships are given in Tables 3, 4 and 5 and Figs 4, 5 and 6, respectively.

The confidence levels (l-P_r), calculated from F-test on eqns (1) (>99·5%), (2) (>96%) and (3) (>94%), indicate that all of the experimental phenomena observed on viscosity, green density and sintered density were adequately described. In the same way, confidence levels (1-P'_r) given by Student's test indicated that the values of the polynomial coefficients had been estimated with a satisfactory accuracy. The sign and value of each coefficient show the effects of powder and deflocculant contents on the measured characteristics.

Powder content appeared as the most influential parameter on both slurry viscosity and green density of cast samples. At low content, only small increases in the relative viscosity were noted with increasing powder content, whereas a strong increase was observed from 65 wt% (Fig. 4), which is in agreement with other authors' results.[33]

Table 2. Slurry viscosity, green and sintered relative densities of 80 vol% HAP–20 vol% Al_2O_3 composites

N°	P%	D%	η(mPa s)	τ_g (% d_{th})	τ_{hp}(% d_{th})
1	70	4	70	44·3	98
2	50	4	22	46·7	90·9
3	65	4·866	40	51·2	98·2
4	55	3·134	25	49·1	96·4
5	65	3·134	35	51	96·4
6	55	4·866	25	49·1	86·9
7	60	4	30	49·9	98·6
7'	60	4	32	/	99·3

Table 3. Statistical analyses for viscosity equation

Validity of eqn (1) (F-test)			P_r (%): 0·2
Sample standard deviation			0·0888
Coefficient	*Standard deviation*	*t (Student)*	P'_r(%)
3·4335	0·0628	54·67	<0·01
0·5202	0·0513	10·17	<1
0·2363	0·0888	2·66	5·7
–0·096	0·0888	–1·08	34·2

Table 4. Statistical analyses for compaction rate equation

Validity of eqn (2) (F-test)			P_r (%): 3·5
Sample standard deviation			1·3134
Coefficient	*Standard deviation*	*t (Student)*	P'_r(%)
49·9	1·3134	37·99	<0·01
–4·4	1·6086	–2·74	5·2
1·7333	1·6086	1·08	34·3

Table 5. Statistical analyses for densification rate equation

Validity of eqn (3) (F-test)			P_r (%): 5·8
Sample standard deviation			1·2619
Coefficient	*Standard deviation*	*t (Student)*	P'_r(%)
98·95	0·892	110·89	<0·01
4·25	0·729	5·83	<5
–2·223	0·729	–3·05	9·2
–4·5	1·262	–3·57	6·9
–4·467	1·262	–3·54	7
6·524	1·457	4·48	<5

For cast samples, compaction rate (τ_g) reached maximum values (about 51% of the theoretical density) at 65 wt% of powder content (Fig. 5). Below 60 wt%, τ_g remained below 50%. This could be explained by the presence of too great a quantity of water to remove during the casting process. Low compaction rates measured at 70 wt% of powder content might result from an increasing difficulty in alumina platelet rearrangement during casting due to the much higher viscosity of the slurry (70 mPa s^{-1} against 35 to 40 mPa s^{-1} at 65 wt%).

The surface response of densification rates (Fig. 6) presented somewhat similar variations to that of compaction rate. However, a simultaneous effect of powder and deflocculant contents was obtained since the concomitant increase of these two variables (corresponding to the term $P \times D$ in eqn (3)) led to increasing densification rates.

SEM observations of hot pressed composites allowed identification of two categories of microstructures:

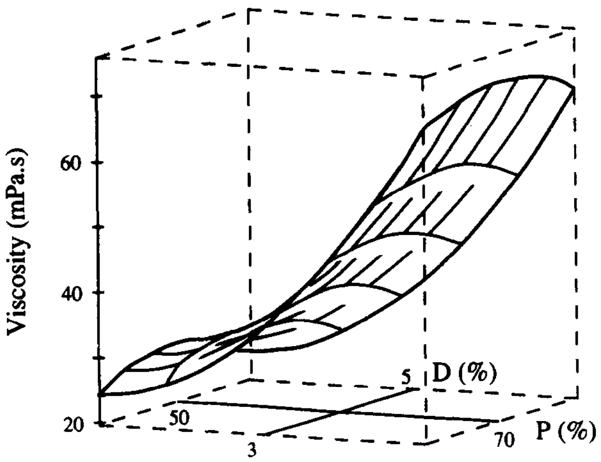

Fig. 4. Graphic representation of viscosity relationship (eqn (1)).

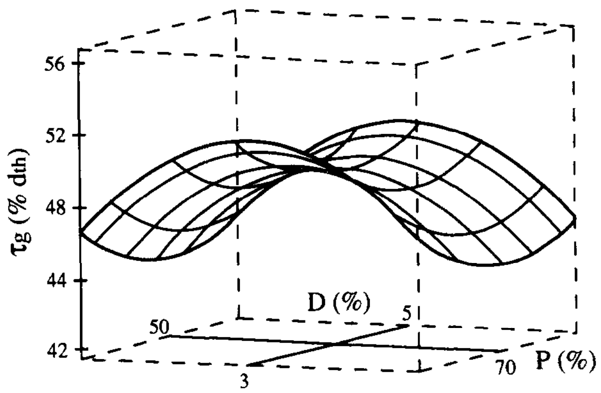

Fig. 5. Graphic representation of compaction rate relationship (eqn (2)).

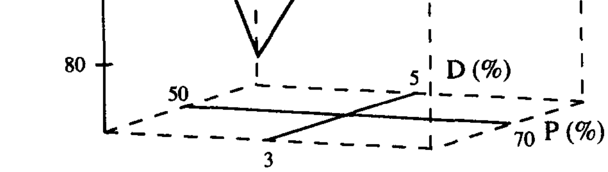

Fig. 6. Graphic representation of densification rate relationship (eqn (3)).

(i) Heterogeneous distribution of platelets within the matrix (Fig. 7), with some platelet clusters, was observed for materials resulting from suspensions containing up to 60 wt% of powder (i.e. experiment nos 2, 4 and 6). This would mean that, because of the low quantity of powder contained in these slurries, deflocculant content was not adjusted to obtain a good dispersion. In this case, and

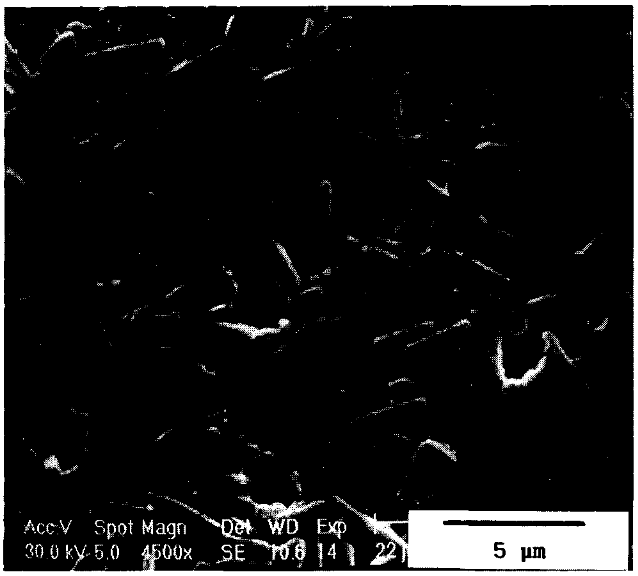

Fig. 7. SEM micrograph of heterogeneous composite.

according to the studies of HAP powder dispersion, a lower deflocculant content should be necessary for an optimal dispersion.[31]

(ii) Homogeneous distribution of platelets resulted from 65 and 70 wt% powder content slurries. A preferred orientation of platelets in parallel planes was observed which resulted from casting and was further enhanced by hot uniaxial pressing. Indeed, platelets tend to lie in planes perpendicular to the direction of the applied stress during hot pressing. This orientation was more important for slurries containing 65 wt% of powder (Fig. 8) than for 70 wt% (Fig. 9). This confirms the poorer rearrangement of alumina discs during the casting process of highly concentrated slurries as previously hypothesised.

Finally, slurries of about 35 to 40 mPa s^{-1} relative viscosity (i.e. containing 65 wt% of powder) appear to be the most suitable ones to obtain optimal casting conditions, high compaction rates and homogeneous hot pressed composites.

3.3 Toughness of hot pressed materials

In view of the previous results, materials containing 0, 10, 20 and 30 vol% of alumina have been produced from the optimal slurry composition (no. 5). As preferred orientation of platelets within the matrix was evident in all the composites, toughness values should depend on the measurement direction. Consequently, K_{IC} has been determined from measurement of the length of indentation cracks in both perpendicular (⊥) and parallel (//) directions to platelet faces as described on Fig. 10.

The development of toughness values versus alumina content is given in Fig. 11. A similar profile of the curves was observed for perpendicular and parallel directions. In both cases, an important increase in toughness values was obtained with platelet incorporation. In comparison with the values measured on the monolithic HAP ($K_{IC\perp}$ = 0·75 (± 0·15) MPa $\sqrt{m}$; $K_{IC//}$ = 0·65 (± 0·20) MPa $\sqrt{m}$), the toughness increased strongly up to 20 vol% alumina ($K_{IC\perp}$ = 2·95 (± 0·45) MPa $\sqrt{m}$; $K_{IC//}$ = 1·95 (± 0.35) MPa $\sqrt{m}$). Then, between 20 and 30 vol%, K_{IC} remained almost constant. This threshold observed above 20 vol% of added alumina agrees with theoretical predictions which indicate an asymptotic toughening at volume fractions in excess of 0·2.[20]

Platelet orientation induced strong anisotropic toughness characteristics. Indeed, the toughening was lower in the parallel direction of crack

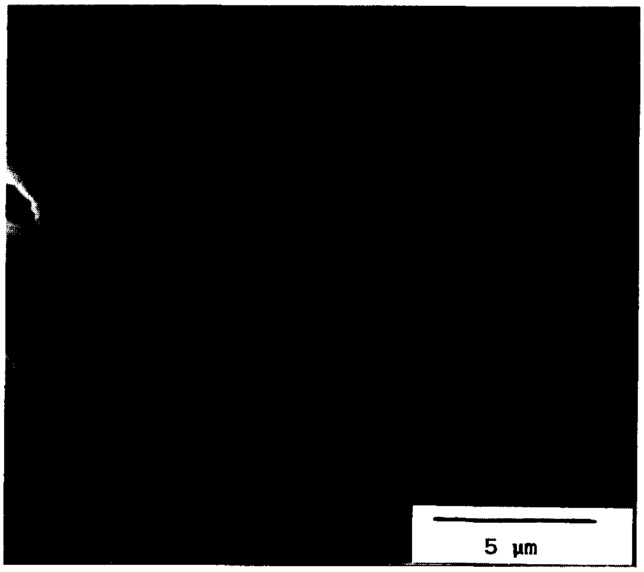

Fig. 8. SEM micrograph of homogeneous composite (slurry: 65 wt% powder content).

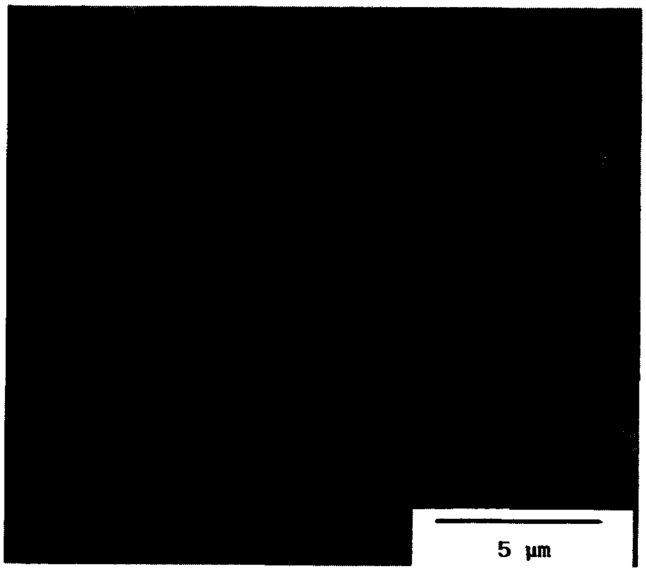

Fig. 9. SEM micrograph of homogeneous composite (slurry: 70 wt% powder content).

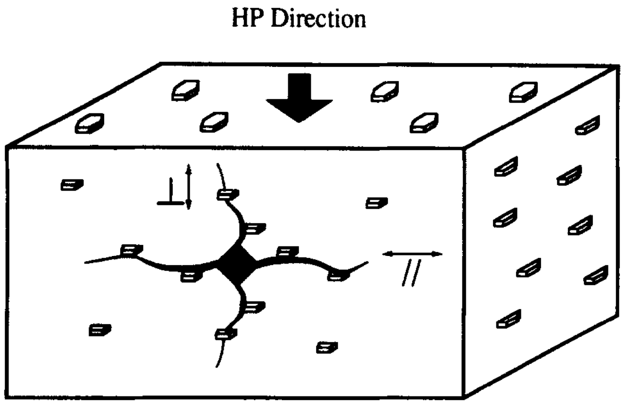

Fig. 10. Schematic representation of indentation crack directions.

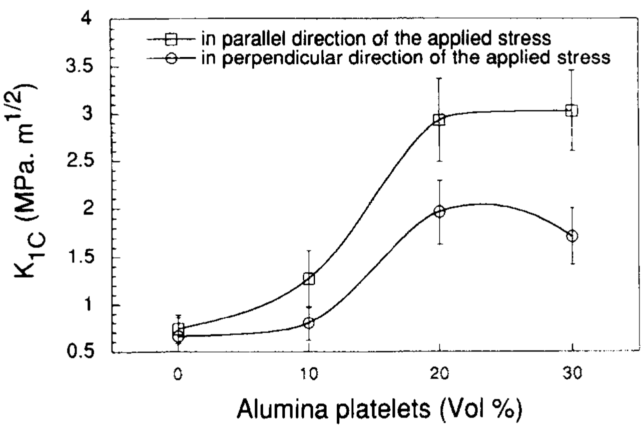

Fig. 11. K_{IC} versus Al_2O_3 content in perpendicular (○) and parallel (□) directions.

propagation than in the perpendicular one. This anisotropy can be explained by energy dissipative mechanisms of crack deflection along platelet faces, platelet debonding and crack bridging involved in the reinforcement and described in details in a previous paper.[19] Thus, platelets are particularly efficient in developing these mechanisms when the crack plane is nearly perpendicular to the platelet faces. Conversely, toughening is logically minimised when the crack plane propagates in the direction parallel to that of platelets. Nevertheless, the values of the measured toughness at 20 vol% of alumina content (close to 3 MPa √m and 2 MPa √m in the perpendicular and parallel directions, respectively) prove the superiority of platelets over particles[16,17] in inducing toughening mechanisms and improving the mechanical reliability.

A good dispersion of the reinforcing phase within the matrix is also of prime importance. The presence of small agglomerates of platelets leads to toughness values, measured by the SENB method (known to give higher values compared with Vickers indentation), of only 2 MPa √m in the perpendicular direction for 20 vol% of Al_2O_3 platelets.[19] For more comparison, composites resulting from compositions nos. 2, 4 and 6, in which some heterogeneities in platelet distribution were observed, exhibited an important drop in toughness since the measured values fell between 1·5 and 2 MPa √m (in the perpendicular direction). Therefore, small heterogeneities constitute critical defects that induce very detrimental effects on the mechanical reliability of these materials.

From this point of view, microstructural observations of composites (Figs 8, 12 and 13) showed that up to 20 vol% of alumina, the platelets were almost totally dispersed whereas for 30 vol% some platelets clusters remained. These clusters, which sometimes could form an interconnected network of platelets (Fig. 13) could constitute critical defects responsible for the threshold observed in toughness increment.

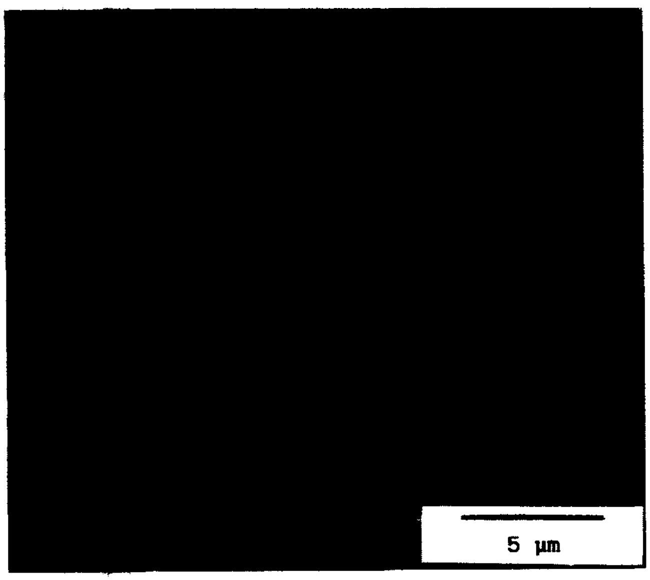

Fig. 12. SEM micrograph of HAP-10 vol% Al_2O_3 composite.

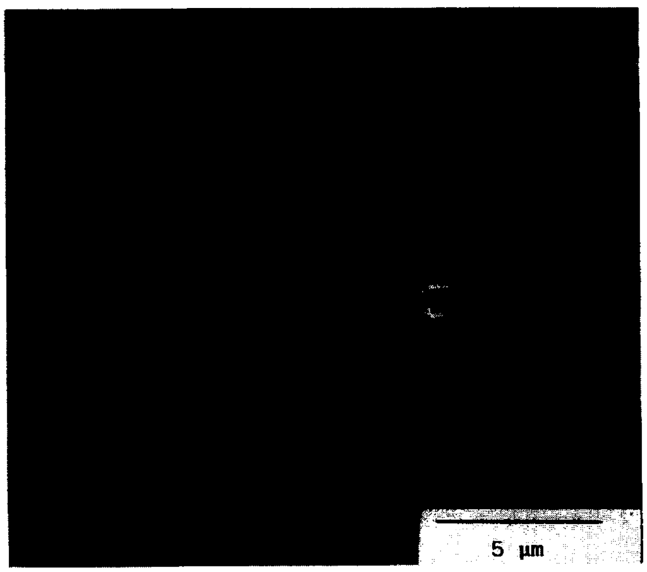

Fig. 13. SEM micrograph of HAP-30 vol% Al_2O_3 composite.

4 Conclusions

This study allowed us to demonstrate that slip casting can be a suitable route to develop reliable alumina platelet-reinforced hydroxyapatite composites. Indeed, pressure filtering of ultradispersed flocced composite suspensions was not totally efficient to remove platelets agglomerates or clusters and resulted in a limited toughening effect with a relative gain in toughness of only 65% at 20 vol% of Al_2O_3.[19] Slip casting of stabilised slurries leads to further improvements. In comparison with the monolithic HAP, the fracture toughness of composites was three to four times higher with 20 vol% of added Al_2O_3. Such enhancement has been achieved only providing a good control of composite microstructure is obtained. To this end, experimental design appears a very useful method of investigation to characterise and quantify the influence of processing parameters. Thus, slurries containing about 65 wt% of composite powder and 3·1 wt% of deflocculant were required to reach optimal dispersion of platelets and mechanical characteristics.

Due to the disc-shaped morphology of the reinforcing phase, platelet orientation in relation to the direction of crack plane propagation is predominant in the toughening increment. In the same way, this increment is strongly dependent on alumina platelet content. In any case, a threshold appears from 20 vol%. Above this content, a change in slurry behaviour is also observed; the flow becomes shear thinning whereas it was quasi-Newtonian for lower amounts. Percolation of alumina platelets is assumed to be responsible for these phenomena.

It must be noted that the influence of thermal treatment conditions on the microstructure, more particularly in relation with grain size of the HAP matrix, as well as the influence of platelet size have not yet been optimised. Thus, further improvements of the mechanical reliability of these composites can be expected.

Finally, in view of these results, alumina platelet-reinforced HAP could constitute promising materials to extend the potential applications as bone substitute.

Acknowledgement

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