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Processing by tape casting and mechanical behaviour of aluminous cement-based matrix alumina fibers composites

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Abstract

The present work concerns the mechanical behaviour of aluminous refractory cement and Fontainebleau sand matrix reinforced by mineral long fibres. The results concern the matrix and 1D stratified composites obtained by tape casting. By using refractory alumina fibres, the effect of fibre reinforcement is evidenced: the 4-points flexural strength is increased by a factor 3 compared to the matrix alone and the mechanical behaviour is non-brittle with a large non linear section.

Keywords: Tape casting; Composites; Mechanical properties; Aluminous cement

1. Introduction

Composite materials made of brittle mineral matrices reinforced by long fibres exhibit original mechanical properties, without the drawback of brittleness.[1] In particular, they can be used as thermostructural ceramic–ceramic composites for applications at high temperatures ($T > 1500\,^{\circ}C$), which generally involve expensive manufacturing processes. Consequently, for wide range of applications, researches are conducted to obtain materials with acceptable thermomechanical properties at lower temperatures (around 1000 °C), using low-cost methods of fabrication.

An attempt of making composites with a refractory alumina cement matrix is reported in this paper. At first, in order to show the feasibility of this processing technique, model composites have been manufactured with a cementitious matrix made of sand mixed with alumina cement, reinforced by very low-cost glass fibres. Of course, these composites have been only tested up to 600 °C, which corresponds to the glass transition temperature of the fibres. The processing method, tape casting, used for making unidirectional composites is described and then, mechanical characteristics of the composites in the temperature range 20–600 °C are reported.

Finally, the application of the process to manufacture composites with refractory alumina fibres shows that refractory materials with interesting non-brittle mechanical behavior can be obtained after heating at 1300 °C.

2. Fabrication of the glass fibres composites

2.1. Raw materials

The aluminous cement is SECAR 71 (Lafarge). The principal mineralogical phases are the monocalcic aluminate $CaAl_2O_4$ (CA) and the calcic bialuminate $CaAl_4O_7$ (CA_2), as shown in Table 1. Grain size ranges between 0.1 and 40 μm with an average diameter = 6 μm.

The matrix is obtained by mixing the cement with Fontainebleau sand which has a grain size lower than 125 μm and an average diameter of 70 μm. The composition of the sand has been analysed by the ICP (inductive coupled plasma) technique. Its major component is silica (Table 2).

A sand content ratio, $M_{sand}/(M_{cement} + M_{sand})$=0.29 has been chosen, since it leads to the best mechanical properties.[2]

For reinforcement, we used glass fibers (CEM-FIL ROVING, Vetrotex) formed by strand of 1200 monofilaments of a diameter between 9 and 14 μm. Tables 3 and 4 give the chemical composition, evaluated by ICP, the main characteristics of the fibres given by the supplier.

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Table 1
Composition of the alumina cement

	Weight%
Phases	
CA	56
CA_2	38
$C_{12}A_7$	<1
A	6
Oxide	
C	28
A	72

C = CaO; A = Al_2O_3.

Table 2
Chemical composition of Fontainebleau sand

Oxide	Weight%
SiO_2	99.60
Al_2O_3	0.30
Fe_2O_3	0.015
Others	0.085

Table 3
Chemical composition of glass fibres

Oxides	Weight%
SiO_2	64.62
ZrO_2	14.65
Na_2O	13.70
Al_2O_3	3.26
Fe_2O_3	1.59
K_2O	1.54
CaO	1.24
FeO	0.19
TiO_2	0.12

2.2. Experimental procedure used for tape casting of composites

Tape casting is classically used to process monolithic ceramic sheets with thickness between 25 and 1000 μm for micro-electronics applications (substrates, multi-layer condensers) and in fuel cells.[3,4] However, the high cost of the deposited raw materials (AlN, Al_2O_3, $BaTiO_3$, Y_2O_3–ZrO_2, ZrO_2), and brittle fracture of final products limit their use. Therefore, the tape casting technique has been adapted to manufacture cement films with interesting properties to be used as electronic substrates.[5] For the manufacture of composites, the casting device has been modified (Fig. 1) to allow the preparation of unidirectional mono-layers (or prepregs).[6]

Table 4
Characteristics of the glass fibres

Tensile strength (20 °C) (MPa)	1700
Young's modulus (20 °C) (GPa)	72
Strain at rupture (20 °C) (%)	2.4
Decomposition temperature (°C)	860

In the particular case of a cementitious matrix, the following steps have been followed:

- casting of a first matrix layer of approximately 400 μm in thickness;
- alignment of a layer of fibres stretched between two combs;
- casting of a second layer with the same thickness than the first one.

After 1 h of hydraulic setting at open air on the support, the mono-layer is hydrated by immersion in water at 20 °C during 96 h, which helps hydration and material consolidation.

The tape is then cut into square 10 cm × 10 cm sheets which are piled up and cemented to each other by a thin film of the same slurry as the one used for tape casting. After hydration, 1D or 2D 0°/90°/0° stratified composites are obtained. By changing the inter-tows distance in the prepregs, it is possible to obtain fibre fractional volume ranging from 1.4% to 15%. With glass fibres, it was found that 11% leads to the best compromise between a good infiltration of the matrix between tows and a good mechanical reinforcement.[2]

2.3. Slurry processing

The preparation of slurries for tape casting is commonly carried out in two stages, namely (a) de-agglomeration and dispersion of powders in the solvent with the aid of the dispersant, and (b) homogenisation of the slurry with plasticizers (Fig. 2). The sequence of additions is critical. The dispersant has to be added before the binder and plasticizers to prevent competitive adsorption. The initial adsorption of the plasticizers and binder

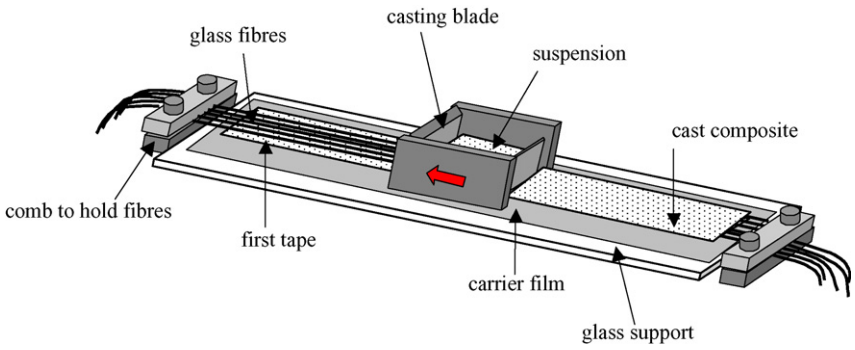

Fig. 1. Principle of the device used for the fabrication of composite layers by tape casting.

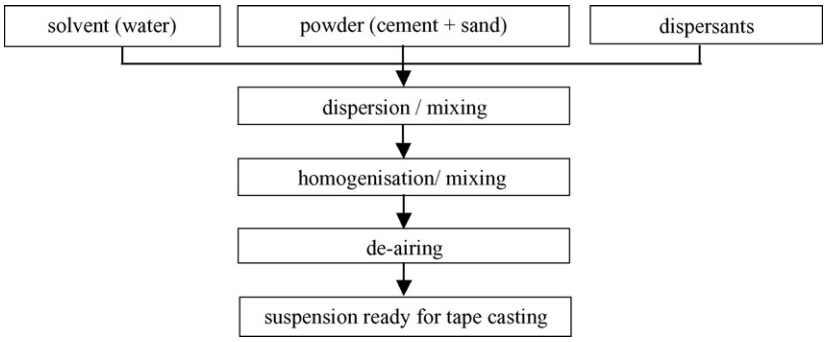

Fig. 2. Schematic diagram for the preparation stages of tape casting suspensions.

on the particle surfaces prevents the dispersant from being subsequently adsorbed, thereby decreasing its effectiveness.[7]

The characteristics of the powders (small particle size, low specific area, multimodal distribution), the concentration of organic products (dispersants and plasticizers) have been adjusted to confer the required rheofluidizing behaviour to the casting slurry.[2] The suspension must present a Newtonian behaviour to easily impregnate the fibre strands, while remaining sufficiently plastic to preserve a homogeneous and regular thickness after casting.

3. Mechanical characteristics of the glass fibres composites

3.1. Flexural tests at room temperature

The mechanical behaviour was measured by monotonic loading under 4-points bending test on parallelepipedic samples (h mm × 20 mm × 100 mm), with length corresponding to fibre axis and where the thickness, h, depends on the type of tested material (matrix tape, mono- or multi-layer composite). The specimen is resting on two supports separated by a distance u. A load, F, is applied at two points, distant of v, symmetrical compared to the middle of the sample. Given the section, $b \times h$, of the specimen, the flexural stress, σ, can be calculated from the applied load, F, as follows:

$$\sigma = \frac{3F(u - v)}{bh^2} \quad (1)$$

In the present study, $u = 60$ mm, $v = 30$ mm.

The flexural strength σ_R is derived from the load value at which the sample breaks. For each sample, at least 10 measurements are carried out and the reported data for σ_R correspond to average values.

Fig. 3 shows results of flexural tests for two materials just after hydration: one corresponds to the matrix alone, and the other to a mono-layer sample. The effect of the reinforcement with fibres is quite obvious: not only the 4-points bending resistance of a mono-layer is increased by approximately a factor 3 compared to that of the matrix, but also the mechanical behaviour curve exhibits a large non-linear section, which is typical of a ceramic–ceramic non-brittle composite. Fig. 4 confirms this result for a 1D double-layers composite. In that case, the stress at which the first cracks appear in the matrix and the strength are more important for the double-layers composite than the mono-layer composite. The strength is increased and reaches 65 MPa, compared to about 15 MPa for the matrix and 50 MPa for the mono-layer composite (Figs. 3 and 4).

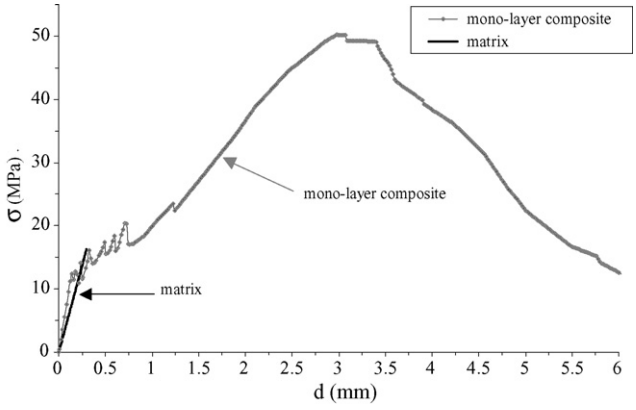

Fig. 3. Flexural behaviour of the matrix and a mono-layer glass fibre composite at 20 °C.

3.2. Evolution of the mechanical properties with temperature

Conversion of hydrates, followed by dehydration, affect the mechanical properties, when temperature is increased from 20

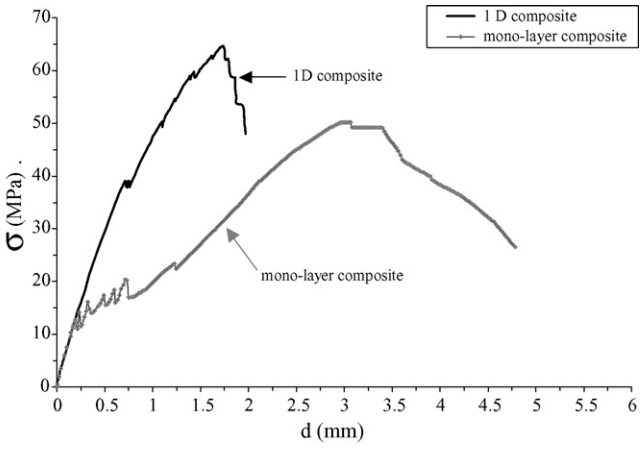

Fig. 4. Flexural behaviour of a mono-layer and an unidirectional 1D double-layer glass fibre composites at 20 °C.

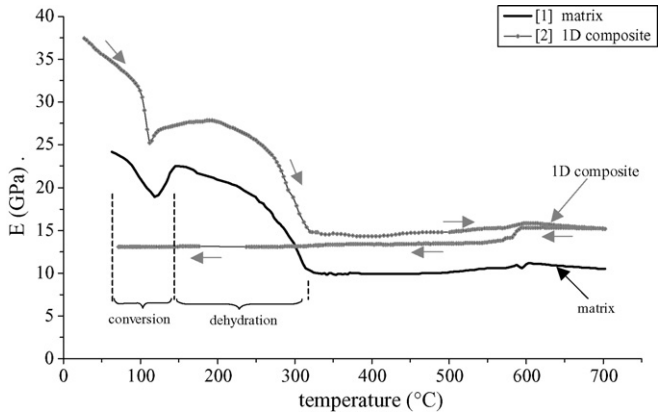

Fig. 5. Young's modulus evolutions vs. T in the matrix (curve 1) and in a 1D glass fibre composite (curve 2).

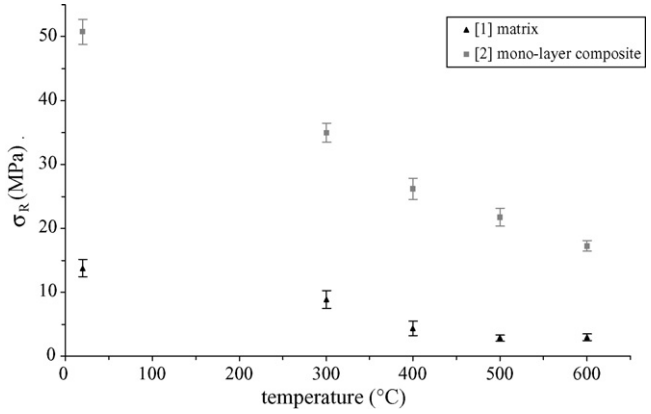

Fig. 6. Flexural strength measured at 20 °C vs. the temperature treatment: (1) case of the matrix; (2) case of the glass fibre mono-layer composite.

to 400 °C.[8] Thus we have studied this effect, first through in situ measurement of Young's modulus by an ultrasonic pulse-echo technique up to 600 °C, second by flexural tests, at 20 °C, on samples that have been previously treated at temperatures between 20 and 600 °C.

The experimental set-up for ultrasonic measurement of Young's modulus at high temperature is described elsewhere.[9] It consists in measuring the velocity of ultrasonic longitudinal waves in long bar mode. In that case the velocity, V_L, is related to the macroscopic Young's modulus of the medium, E, by equation:

$$V_L = \left(\frac{E}{\rho}\right)^{1/2} \tag{2}$$

where ρ is the density of the material.

Samples consist of parallelepipedic bars (120 mm in length, lateral dimensions optimised according to the thickness of the plates and ultrasonic propagation conditions).

The velocity at a given temperature, T, is determined by the measurement of the round-trip time (τ) between successive ultrasonic echoes in the sample:

$$V_L = \frac{2L(T)}{\tau(T)} \tag{3}$$

where L is the length of the sample.

Thus, when the length and the mass of the material change during heating, because of thermal expansion and chemical reactions, corrections have to be made from dilatometric and thermogravimetric experiments. Therefore, the relative variation of Young's modulus at temperature, T, can be written as follows:

$$\frac{E(T)}{E_0} = \left(\frac{\tau_0}{\tau}\right)^2 \left(1 - \frac{\Delta L(T)}{L_0}\right) \left(1 + \frac{\Delta m(T)}{m_0}\right) \tag{4}$$

where the suffix 0 is related to the values at room temperature, $\Delta L/L_0$ and $\Delta m/m_0$ are the variations, between room temperature and T, of length and mass, respectively.

Fig. 5 shows the evolution of Young's modulus E, in samples of matrix alone (curve 1). Two effects have to be noted:

- a deep increase between 125 and 175 °C which corresponds to the stiffening of the cementitious phase during the conversion of hydrates;
- then, above 175 °C, an important decrease of E related to dehydration which involves a multicracking of the cementitious phase and decohesions around the sand particles. After 350 °C, E remains low (10 GPa).

These effects are also observed in the 1D composite (curve 2), but the modulus is higher (about 50%) for the composite because of the presence of fibres.

The decrease of mechanical properties after dehydration is confirmed by the decrease of the measured strength at 20 °C after heat treatments up to 600 °C (Fig. 6). Nevertheless it is important to note the strong effect of the fibre reinforcement: while after heating at 400 °C, the strength of the matrix drops to a very low value (<5 MPa), the strength of the 1D composite is maintained at more than 25 MPa after the same treatment.

4. Results for alumina fibres composites

4.1. Processing

The chosen fibres were refractory NEXTEL 610 alumina (3 M) formed by strand of 750 monofilaments of a diameter between 10 and 12 μm. Table 5 gives the chemical composition, the main mechanical properties at room temperature and the decomposition temperature of the fibres given by the supplier.

Processing of prepregs and composites is similar to the case of reinforcement by glass fibres. The volumic fraction of alumina fibres in prepregs is 15%, which was found to be the best compromise between a good rheological behavior of

Table 5
Characteristics of the alumina fibres

Tensile strength (20 °C) (MPa)	3100
Young's modulus (20 °C) (GPa)	380
Chemical composition	>99 wt.% Al_2O_3
Density (g cm^{-3})	3.9
Decomposition temperature (°C)	2000

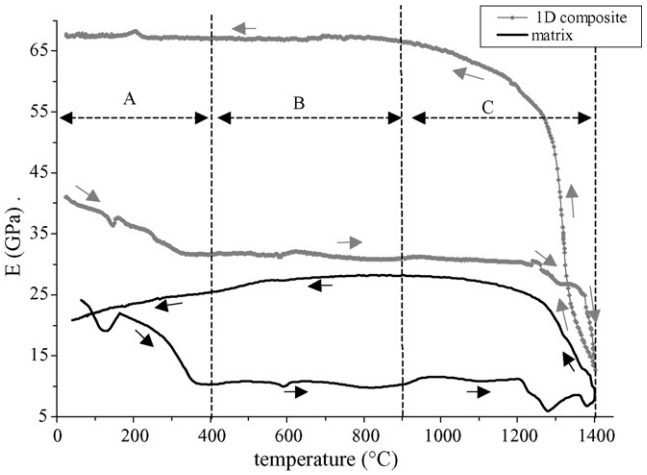

Fig. 7. Young's modulus evolutions vs. T in the matrix (curve 1) and in a 1D alumina fibre composite (curve 2).

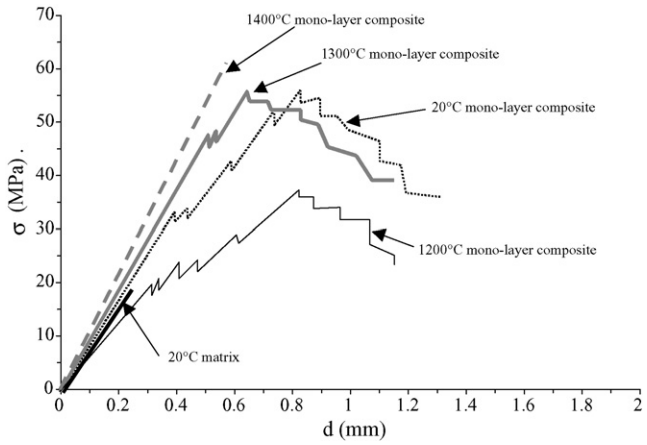

Fig. 8. Results of 4-points tests at 20 °C in hydrated matrix, hydrated composite, and in composites after heat treatments 1/2 h at 1200, 1300 and 1400 °C.

the slurry for tape casting and a reasonable infiltration of the fibres.[2]

4.2. Mechanical properties

Measurements have been performed by using the same experimental techniques as for glass composites.

Fig. 7 shows the evolution with temperature, up to 1400 °C, of Young's modulus in a 1D double-layers composite and in the matrix alone. Three regions can be distinguished:

(A) from 20 to 400 °C, where the effects associated to conversion and dehydration in the cementitious phases are similar to those previously observed in matrix and glass composites (Fig. 5);
(B) after 400 °C, as well as it was observed in the case of experiments performed in Fig. 5, E remains at a very low value corresponding to the dehydrated state of the matrix;
(C) above 900 °C where specific effects appear both in matrix and composites.

This high temperature domain is characterized by E variations related to

(1) Microstructural transformations in the matrix. A slight increase above 900 °C due to CA crystallisation, followed by a deep decrease between 1200 and 1280 °C, associated to the fusion of an eutectic glassy phase in the C–A–S diagram.[2] These effects are also observed in the composite, but with lower amplitudes, because of the high modulus fibres reinforcement.
(2) Phase transformations and sintering mechanisms in the matrix or/and in the fibres. Above 1280 °C, two concurrent phenomena occur in the material: sintering which involves an increase of Young's modulus which is particularly observed in the matrix, but is smoothed in the composite; then, after 1360 °C a decrease of E which is more important is the composite than in the matrix. This is explained by the influence of alumina fibres which favours the formation of an eutectic glassy phase in the pseudo-binary phase CA–S diagram.[2]

When cooling, a strong increase of E, down to 1000 °C denotes that stiffening mechanisms occurred at high temperature: healing of cracks by glassy phase and crystallisation of phases with high modulus (CA, CA_2, CAS_2, C_2AS) which have been detected by XRD after heat treatment and sintering. Furthermore the increase is more important in the composite than in the matrix because of the diffusion of alumina which leads to the formation of CA_6, which was not detected in the matrix.[2]

Below 1000 °C, E regularly decreases in the composite, which shows that the material has a stable microstructure.[9] Young's modulus at room temperature in the sintered composite is higher (68 GPa) than in the just hydrated state (40 GPa). In the matrix, E slightly decreases below 1000 °C, because of cracking on cooling because of internal stresses caused by thermal expansion mismatch between the constituents. In the case of composites, this effect seems to be limited by fibres which put the matrix in axial compression when cooling, because of their CTE (8×10^{-6}) higher than that of the matrix (6×10^{-6}).

Moreover, 4-points flexural tests have been performed at room temperature in materials hydrated and treated at temperatures ranging from 1200 to 1400 °C. The mechanical behaviour curves reported in Fig. 8 and maximum stress at the rupture in Fig. 9 enhance the following points:

- As for fibre glass reinforced composites, the effect of the reinforcement with fibres is efficient: the 4-points bending strength of the hydrated 1D composite is strongly increased compared to that of the matrix and the mechanical behaviour curve exhibits a large non-linear section, which is typical of a ceramic–ceramic non-brittle composite.
- After treatments at 1200–1300 °C, a composite behaviour is still observed in the two cases but, at 1200 °C, the strength decreases because of the week mechanical properties of the matrix, though at 1300 °C the strength is increased close to

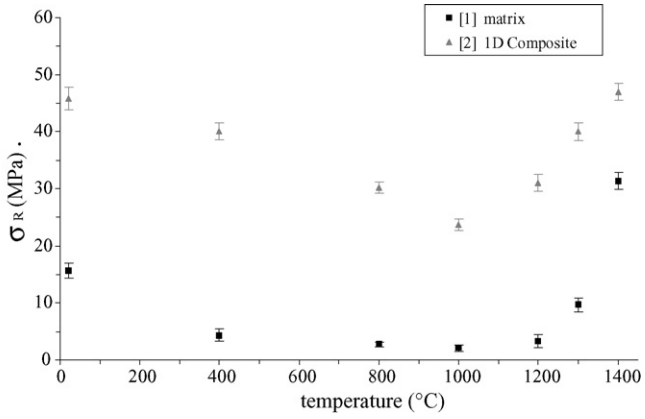

Fig. 9. Flexural strength measured at 20 °C vs. the temperature treatment: (1) case of the matrix; (2) case of the alumina fibre mono-layer composite.

the initial value of an hydrated composite, but with a higher stiffness because of sintering as discussed above.

- The flexural curve after a treatment at 1400 °C, though exhibiting a high stiffness, as expected from results of Fig. 7, and a high strength, is characteristic of a brittle material.

5. Conclusion

These results show that it is possible to manufacture, by tape casting, fibrous composites with a low-cost cementitious matrix, presenting a non-brittle mechanical behaviour and keeping a good level of strength after dehydration. Moreover, by using alumina fibres, it has been shown that refractory composites can be obtained by consolidation of the matrix at 1300 °C. Nevertheless, further work has to be made in order to test the mechanical behaviour at high temperature (up to 1200 °C) and to study the fibre–matrix interfacial properties which are fundamental for the achievement of good mechanical properties in thermostructural composites.

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