$KMg_2AlSi_4O_{12}$ phyllosiloxide as potential interphase material for ceramic matrix composites

Part 1 *Chemical compatibility*

P. REIG, G. DEMAZEAU
Institut de Chimie de la Matière Condensée de Bordeaux – CNRS, Avenue du Dr. Schweitzer, 33608 Pessac Cedex, France

R. NASLAIN
Laboratoire des Composites Thermostructuraux, UMR-47 (CNRS-SEP-Université Bordeaux I), 3 Allée de la Boétie, 33600 Pessac, France

$KMg_2AlSi_4O_{12}$ is a phyllosiloxide isostructural with phlogopite mica, but totally free of OH^- ions. It decomposes at $\approx 950\,°C$ at atmospheric pressure but remains stable up to at least $1350\,°C$ under high pressures. Its chemical compatibility with α-alumina, $MgAl_2O_4$ spinel, forsterite, β-SiC and borosilicate glass selected as representative of fibres and matrices in ceramic matrix composites (CMCs), has been assessed via annealing experiments on multilayers and particulate composites at $900–1200\,°C$. At $T = 900\,°C$ and $P = 100$ MPa, the phyllosiloxide is chemically stable with respect to all the ceramics. At higher temperatures, interdiffusion occurs with the formation of various reaction products. At $T = 1050\,°C$ and $P = 2$ GPa, the extent of the reaction zone is larger for both α-alumina and forsterite than for spinel and β-SiC, whereas at $1200\,°C$, the reactivity of the phyllosiloxide with all the ceramics becomes about the same. Borosilicate glass with a softening point lower than the decomposition onset of $KMg_2AlSi_4O_{12}$ at relatively low pressures seems to be an ideal model matrix material for assessing the potential of the phyllosiloxide as an interphase material in CMCs.

1. Introduction

In ceramic matrix composites (CMCs), a material with a layered crystal structure or a layered microstructure often referred to as the interphase, is used to control the load transfer between the matrix and the fibres as well as the deflection of the matrix microcracks from mode I, i.e. perpendicular to the fibre axis (the load being applied along the fibres) to mode II, i.e. parallel to the fibre surface. The most commonly used interphase materials, e.g. in SiC/SiC or SiC/glass-ceramic composites, are pyrocarbon and hex-boron nitride [1, 2]. However, pyrocarbon and to a lesser extent boron nitride, are sensitive to oxidation (the onset of oxidation being, respectively, ≈ 450 and $\approx 850\,°C$). Refractory oxides exhibiting a crystal structure in which the layers are only weakly bonded to each other (as in graphite or hex-BN) and chemically compatible with both the fibres and the matrix, will be ideal interphase materials in CMCs that have to withstand long exposures at high temperatures in oxidizing atmospheres. Attempts have been made to use micas (e.g. fluorophlogopite) [3], β-alumina-type oxide (e.g. magneto-plumbite) [4, 5] or phosphates (e.g. monazite) [6]. Actually, none of these oxides fully satisfies all the interphase requirements.

A new family of layered oxides called phyllosiloxides, derived from the phyllosilicates via anionic/cationic substitutions has been designed and prepared according to an original route, combining a sol–gel synthesis and a solvothermal treatment of the gel [7]. As an example, the $KMg_2AlSi_4O_{12}$ phyllosiloxide formally derives from the phlogopite mica, $KMg_3(Si_3Al)O_{10}(OH)_2$, via the following anionic/cationic substitution: $2OH^- \rightarrow 2O^{2-}$ and $Mg^{2+} \rightarrow Al^{3+}$ in octahedral O_h sites; $Al^{3+} \rightarrow Si^{4+}$ in tetrahedral T_d sites. The preparation of $KMg_2AlSi_4O_{12}$ was successfully achieved in two steps: (i) a sol–gel synthesis from the corresponding metal alkoxides, and (ii) a solvothermal post-treatment of the resulting gel (with the remaining solvent being in the supercritical state). Analyses by X-ray diffraction (XRD), infrared spectroscopy (IRS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and ^{29}Si-nuclear magnetic resonance (^{29}SiNMR) have shown that the resulting $KMg_2AlSi_4O_{12}$ oxide actually displays a layered crystal structure similar to that of phlogopite without any OH^- anions, silicon being exclusively located in the T_d sites [8, 9]. Consequently, the thermal stability of the $KMg_2AlSi_4O_{12}$ phyllosiloxide has been observed

to be much higher than that of the isostructural phlogopite, the phyllosiloxide being stable up to ≈ 950 °C at atmospheric pressure and up to at least 1350 °C under a pressure of 2 GPa, whereas phlogopite is known to decompose at about 500–700 °C at atmospheric pressure [10].

The aim of the present study, whose results are presented as two companion papers, was first to explore the potential of the $KMg_2AlSi_4O_{12}$ phyllosiloxide in terms of chemical compatibility with materials representative of ceramic fibres and matrices and, second, to try to establish via preliminary experiments performed on model composites whether it can actually act as interphase [11].

2. Experimental procedure

Based on a literature survey and on the fibres commonly used in CMCs, the following materials were selected: (i) alumina (α-Al_2O_3), forsterite (Mg_2SiO_4), spinel ($MgAl_2O_4$), silicon carbide (β-SiC) and a borosilicate glass (Pyrex) (main oxide constituents SiO_2 80 wt %, B_2O_3 13.1 wt %, Na_2O 3.5 wt %), as representative of the matrix, and (ii) alumina (α-Al_2O_3) and silicon carbide (β-SiC) as representative of the fibres.

The nature of the samples used to test the chemical compatibility of the phyllosiloxide with the CMC constituents listed above and their preparation conditions have been selected on the basis of the two following considerations. First, the chemical compatibility had to be studied in temperature–pressure conditions close to those actually used in the processing of the corresponding CMCs. In the processing of CMCs according to the chemical vapour infiltration process (CVI), the temperature and the pressure fall usually within the ranges 900–1000 °C and a few kPa to 100 kPa, respectively [12]. Furthermore, the processing of glass-ceramic matrix composites is usually performed at 1000–1300 °C and 50–100 MPa depending on the composition of the glass ceramic matrix [13]. Second, and as already mentioned, the decomposition temperature onset of the $KMg_2AlSi_4O_{12}$ phyllosiloxide depends upon the pressure [10].

Two types of test sample and preparation conditions, were selected: multilayer materials prepared by hot-pressing, and particulate composites prepared in a belt apparatus. The multilayer consists of a layer of phyllosiloxide powder between two ceramic slabs (or two ceramic powder layers), one representative of the fibre and the other of the matrix, as schematically shown in Fig. 1a. The multilayer was set in the graphite die of a uniaxial hot-pressing apparatus. Because the applied stress has to be limited to 100 MPa (the highest stress compatible with the graphite tooling), the experiments were performed at a temperature (typically 900 °C) slightly below the decomposition onset of the phyllosiloxide at relatively low pressures (Table I) [10]. Conversely, the annealing duration under pressure was sufficiently long (from 1–8 h) in order to yield interfacial diffusion zones large enough for X-ray spectroscopy analysis by electron probe micro-analysis (EPMA). Furthermore, long annealing times were

(a)   Compression axis
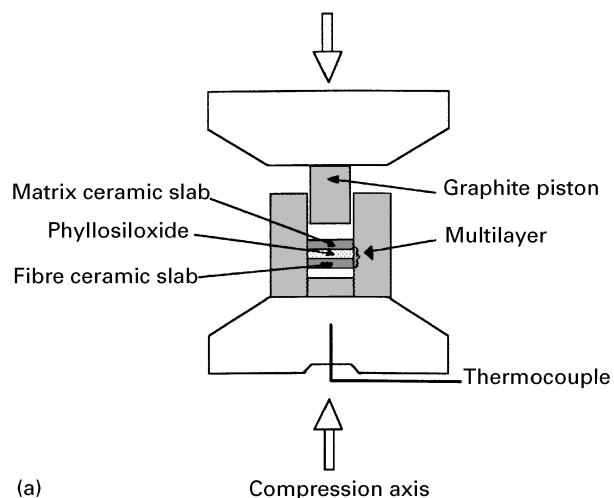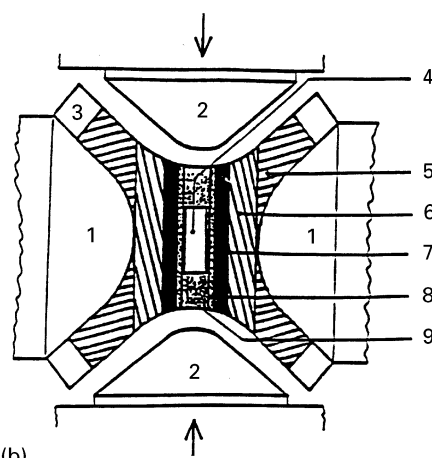
(b)

Figure 1 (a) Hot-pressing apparatus and (b) belt apparatus: 1, tungsten carbide die; 2, tungsten carbide pistons; 3, teflon joints; 4, gold capsule with particulate composite; 5, 6, pyrophylite joints; 7, graphite neurofurnace; 8, alumina tube; 9, lanthanum oxide.

TABLE I Nature of the ceramic/phyllosiloxide/ceramic multi-layers and their processing conditions

Sample	Ceramic layers[a]		Hot-pressing conditions		
	1	2	T (°C)	P (MPa)	t (h)
1	s(slab)	s(slab)	900	100	2
2	s(slab)	s(slab)	900	100	8
3	s(powder)	s(powder)	900	100	2
4[b]	s(slab)	s(slab)	900	30	0.25

[a] s, Spinel
[b] Phyllosiloxide mixed with 80 SiC_2–13B_2O_3–3.5 Na_2O glass.

assumed to favour the densification of the phyllosiloxide powder under pressure and to result in some adhesion between the ceramic slabs and the phyllosiloxide layer. The processing conditions are also listed in Table I. The particulate composites were prepared by mixing ceramic particulates (a few 100 μm in size) with the phyllosiloxide powder. The mixture was set in a small gold tube (diameter 3 mm, length 10 mm, sample weight ≈ 120 mg) which was then sealed. The tube was set in a belt apparatus, as schematically shown in Fig. 1b, and annealed up to

$\approx 1350\,°C$ under a pressure of 2 GPa for durations up to 2 h. Under such conditions, the phyllosiloxide was known to be stable [10].

After annealing, each sample was cut with a diamond saw, mounted in an epoxy resin, and polished according to the conventional method. The interfacial zone between the phyllosiloxide and the ceramic material was analysed by EPMA, the results being shown as diffusion profiles. Finally, the formation of new phases was assessed by XRD (CuK_α).

3. Results and discussion
3.1. Interfacial reactions at 900 °C in multilayers

The first experiments were performed with multilayers (sample 1) consisting of a layer of phyllosiloxide powder inserted between two sintered ceramic slabs of spinel $MgAl_2O_4$, annealed at 900 °C under 100 MPa for 2 h (Fig. 1a and Table I). Under such conditions, it was impossible to characterize the interfacial zones, owing to the absence of adhesion between the phyllosiloxide layer and the spinel slabs. Presumably, at such a low temperature, the interdiffusion coefficients were too low to yield significant interactions. Using the same P, T hot-pressing conditions, a second experiment was performed with a much longer annealing duration, i.e. 8 h instead of 2 h (sample 2). Despite the low temperature, the increase of the annealing duration was large enough to result in sufficient interfacial bonding (diffusion phenomena at a given temperature are known to depend on the square root of time). Thus, the sample could be cut and polished for chemical analysis by EPMA. An example of a diffusion profile recorded across the spinel/phyllosiloxide interface in a spinel/phyllosiloxide/spinel multilayer is shown in Fig. 2. The apparent thickness of the interfacial zone is of the order of 1–2 µm but no deconvolution of the signals has been performed suggesting that the actual thickness might be lower. On the spinel side of the diffusion couple, the weight percentages of MgO and Al_2O_3 are close to those of $MgAl_2O_4$ (MgO 23.33 wt % and Al_2O_3 71.67 wt % theoretical). On the phyllosiloxide side, all the elements of the phyllosilox-

ide are actually present with weight percentages in reasonable agreement with the theoretical values (SiO_2 57.35%, MgO 19.24%, Al_2O_3 12.17%, K_2O 11.24%), the SiO_2 and K_2O percentages, however, being low. It appears from these results that the interactions between the spinel and the phyllosiloxide were limited and the interface relatively sharp, as expected from the low value of the temperature. Finally, replacing in the multilayer the sintered spinel slabs by layers of spinel powder (sample 3), yielded samples with more reactive interfaces. After annealing at $T = 900\,°C$, $P = 100$ MPa and $t = 2$ h, the interaction zone at the spinel/phyllosiloxide interface had a thickness of about 6 µm. This apparent increase of the interaction zone thickness could be explained by the fact that (i) the spinel did not sinter during hot pressing (the sintering temperature for $MgAl_2O_4$ being of the order of 1400 °C, i.e. far beyond the hot-pressing temperature) and (ii) the interface was not plain but displayed some roughness (related to the grain size of the spinel powder).

Experiments were also performed with multilayers (sample 4) consisting of a layer of a mixture of phyllosiloxide powder and borosilicate glass powder between two sintered ceramic slabs (Fig. 1a and Table I). This specific glass was selected for its low softening point (i.e. $\approx 800\,°C$, thus lower than the decomposition onset of the phyllosiloxide) and for its ability to be easily densified by hot-pressing under low PT conditions. As expected, dense samples with good interfacial adhesion were obtained after short annealing (typically 15 min) at $T = 900\,°C$ and $P = 30$ MPa. EPMA diffusion profiles across the glass/phyllosiloxide and glass/spinel interfaces, are shown in Fig. 3. The glass/spinel interface is relatively sharp (thickness less than 1 µm) suggesting the occurrence of interactions of limited intensity. Conversely, there seems to be a relatively broad interaction zone between the borosilicate glass and the phyllosiloxide particles even after such a short annealing duration. However, this broad interphase might not be a true interdiffusion zone but a zone resulting from the infiltration of the liquid glass in the pores of the phyllosiloxide. For such annealing conditions (i.e. low temperature and short time), an extended interdiffusion is unlikely. It thus appears that the use of a phyllosiloxide interphase will be compatible at least in a first approximation with a borosilicate matrix, owing to the low softening point of this specific glass and the high enough thermal stability of the phyllosiloxide.

3.2. Interfacial reactions at high temperatures in particulate composites

Interaction phenomena rate-controlled by diffusion are enhanced by an increase of the temperature. However, and as already mentioned, the phyllosiloxide is no longer stable beyond $\approx 950\,°C$ under a pressure of about 100 kPa. In order to raise the temperature, the annealing experiments should be performed under higher pressure (which in turn increases the diffusion coefficients). Particulate composites for EPMA analysis and powder mixtures for XRD characterization
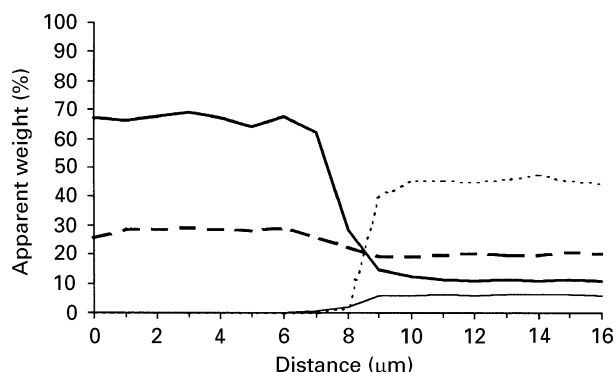

Figure 2 Interdiffusion profiles recorded across the spinel/phyllosiloxide interface in a spinel/phyllosiloxide/spinel multilayer ($P = 100$ MPa, $T = 900\,°C$, $t = 8$ h) by EPMA. (– –) MgO, (——) Al_2O_3, (- - -) SiO_2, (—) K_2O.

were annealed at a pressure of about 2 GPa within the temperature range 900–1200 °C in the belt apparatus (Fig. 1b). No attempt was made to optimize the value of the pressure (i.e. the phyllosiloxide may well be stable under lower pressure within this temperature range).

An example of EPMA characterization of the interaction phenomena at the particulate/phyllosiloxide interface is shown in Fig. 4 for the α-alumina/phyllosiloxide particulate composite. As temperature is raised from 900 °C to 1200 °C at constant annealing duration, the width of the interaction zone increases (Table II), a feature which suggests that the interactions are controlled by diffusion. Additionally, the XRD spectrum of a phyllosiloxide/α-alumina mixture treated in the same conditions, shows that the main resulting product is the spinel $MgAl_2O_4$ (Fig. 5a).

Similar experiments were performed on the other particulate composites. The EPMA data in terms of interaction zone width are shown in Table II. At 900 °C, and as already discussed in Section 3.1, the interactions between the ceramic particulates and the surrounding phyllosiloxide remain very limited, whatever the nature of the ceramic particulates. The interface is sharp with interaction zone widths ($\approx 2 \, \mu m$) of the order of the EPMA space resolution. Conversely, at 1050 °C, the interactions are limited for both the spinel/phyllosiloxide and silicon carbide/phyllosiloxide composites but extended for the α-alumina/phyllosiloxide and forsterite/phyllosiloxide composites.
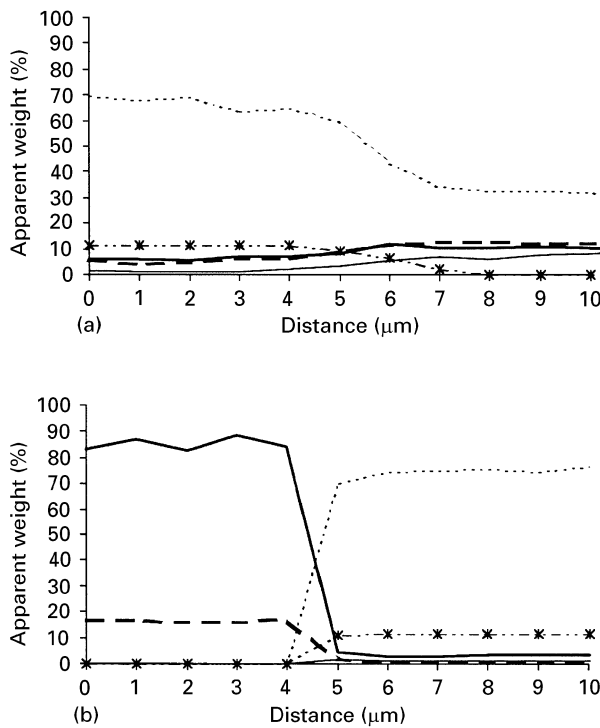
Figure 3 Semi-quantitative interdiffusion profiles across the (a) glass/phyllosiloxide and (b) glass/spinel interfaces in spinel/pyrex + phyllosiloxide/alumina multilayer ($T = 900$ °C, $P = 30$ MPa, $t = 15$ min) as recorded by EPMA. (– –) MgO, (——) Al_2O_3, (- - -) SiO_2, (—) K_2O, (—–∗—–) B_2O_3.
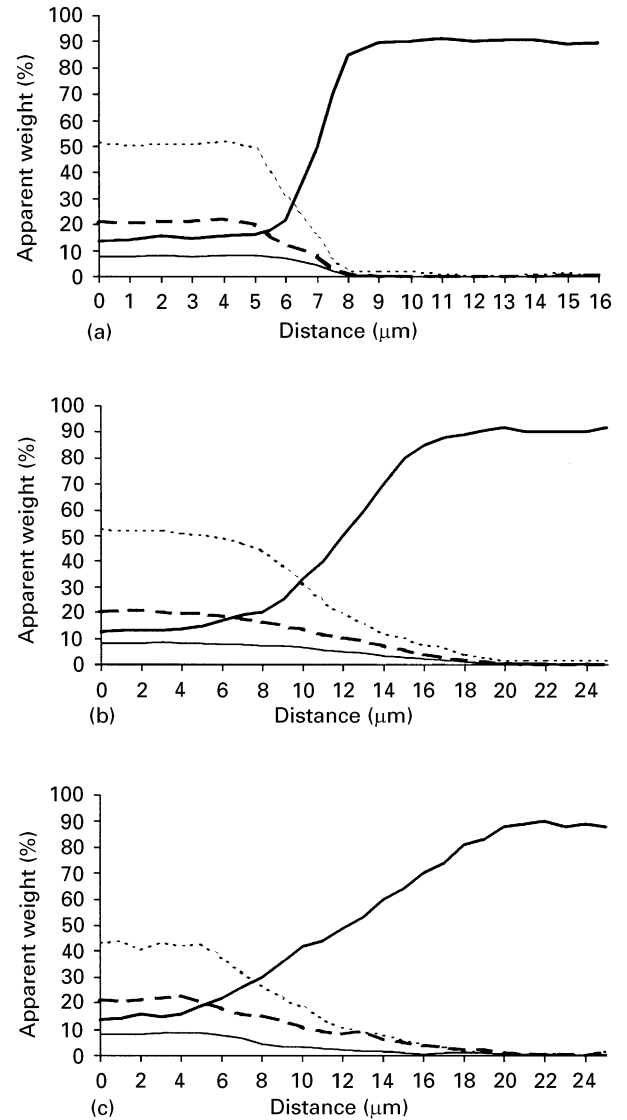
Figure 4 EPMA diffusion profiles recorded across the ceramic/phyllosiloxide interfacial zone in α-alumina/phyllosiloxide particulate composites annealed under a pressure of 2 GPa for 2 h at (a) 900 °C, (b) 1050 °C and (c) 1200 °C. (– –) MgO, (——) Al_2O_3, (- - -) SiO_2, (—) K_2O.

TABLE II Width of the interaction zone at the phyllosiloxide/ceramic interface in phyllosiloxide/ceramic particulate composites annealed under 2 GPa for 2 h at increasing temperatures

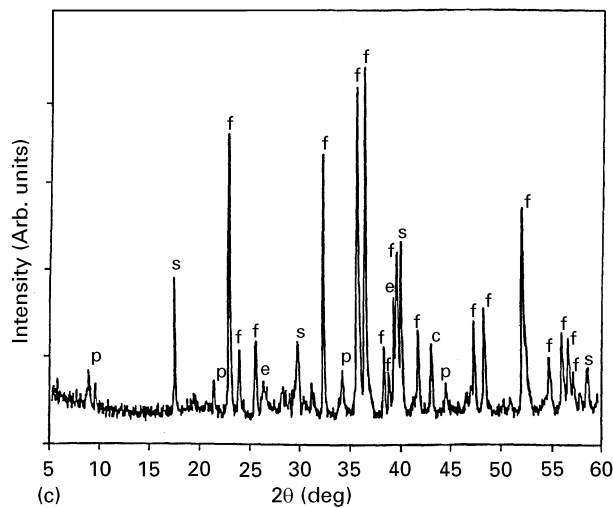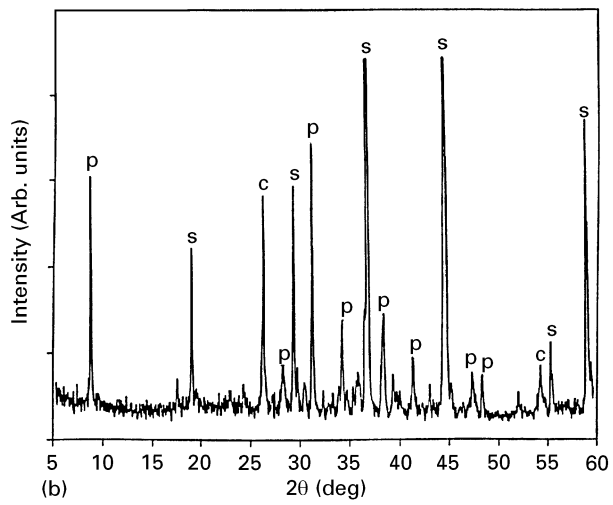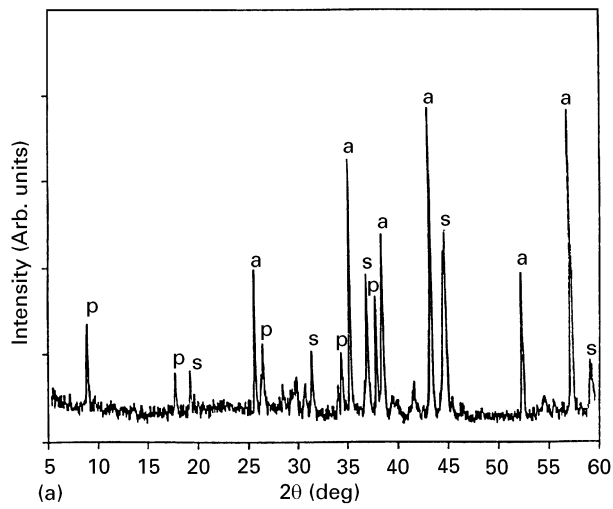| Temperature (°C)	Interaction zone width (μm)			
	Spinel, $Mg_2Al_2O_4$	α-Alumina, Al_2O_3	Forsterite, Mg_2SiO_4	Silicon carbide, β-SiC
900	2	2	2	2
1050	6	14	15	5
1200	16	17	16	16

(a)

(b)

Figure 5 XRD spectra of ceramic/phyllosiloxide powder mixture annealed at $T = 1200\,°C$, $P = 2\,GPa$, $t = 2\,h$: (a) α-alumina/phyllosiloxide, (b) spinel/phyllosiloxide, (c) forsterite/phyllosiloxide (CuK_α wavelength). p = KMg$_2$AlSi$_4$O$_{12}$, a = α-Al$_2$O$_3$, s = MgAl$_2$O$_4$, c = Mg$_2$Al$_4$Si$_5$O$_{18}$, f = Mg$_2$SiO$_4$, e = MgSiO$_3$.

Finally, for 1200 °C all the ceramic materials display almost the same reactivity with the phyllosiloxide.

The nature of the main reaction products was assessed by XRD analysis performed on powder mixtures which have been annealed at $T = 1200\,°C$,

TABLE III Crystallized phases after reaction between phyllosiloxide (KMg$_2$AlSi$_4$O$_{12}$) and ceramics powders ($P = 2\,GPa$, $T = 1200\,°C$, $t = 2\,h$)

Powder mixture	Phase after annealing	XRD spectrum
Phyllosiloxide (KMg$_2$AlSi$_4$O$_{12}$) + α-alumina (Al$_2$O$_3$)	Phyllosiloxide, alumina + spinel	Fig. 5a
Phyllosiloxide (KMg$_2$AlSi$_4$O$_{12}$) + spinel (MgAl$_2$O$_4$)	Phyllosiloxide, spinel + cordierite (Mg$_2$Al$_4$Si$_5$O$_{18}$)	Fig. 5b
Phyllosiloxide (KMg$_2$AlSi$_4$O$_{12}$) + forsterite (Mg$_2$SiO$_4$)	Phyllosiloxide, forsterite + spinel, cordierite, enstatite (MgSiO$_3$)	Fig. 5c

$P = 2\,GPa$ and $t = 2\,h$ (Fig. 5). The interdiffusion between the phyllosiloxide and the ceramic particulates yields (i) spinel MgAl$_2$O$_4$ for the α-alumina/phyllosiloxide mixture, (ii) cordierite Mg$_2$Al$_4$Si$_5$O$_{18}$ for the spinel/phyllosiloxide mixture, and (iii) a mixture of spinel, cordierite and enstatite (MgSiO$_3$) for the forsterite/phyllosiloxide mixture (Table III). It is noteworthy that no crystallized phase containing potassium is present in the reaction products. This feature suggests that potassium may have migrated from the interaction zone, possibly in the gas phase. However, in all the experiments, phyllosiloxide is still present in the mixture after the annealing treatment, showing that a significant portion of potassium has remained in the material. In their study of the interactions between related fluorophlogopite (KMg$_3$Si$_3$AlO$_{10}$F$_2$)/ceramic mixtures, Cooper and Hall have also demonstrated that the diffusion of potassium seems to play an important role in the corrosion of the ceramic particulates [2].

Our experimental data show that the phyllosiloxide KMg$_2$AlSi$_4$O$_{12}$ is compatible with all the ceramic materials representative of fibres and/or matrices which have been considered here, at temperatures lower than 1000 °C. From this point of view, the treatment by CVI of fibre performs coated with KMg$_2$AlSi$_4$O$_{12}$ could be envisaged (disregarding the chemical reactions that might occur, between the phyllosiloxide and the gas phase). Conversely, interactions between the phyllosiloxide and both the fibres and the matrices will occur at temperatures used in the hot-pressing process of CMCs (typically 1200–1400 °C for glass-ceramic matrices). However, and as shown elsewhere [10], phyllosiloxide are highly tailorable materials. Thus, for a given fibre/matrix couple, there might exist a specific phyllosiloxide displaying an acceptable compatibility for this particular couple.

4. Conclusion
The phyllosiloxide KMg$_2$AlSi$_4$O$_{12}$, isostructural with phlogopite but which does not contain any OH$^-$ ions, is chemically compatible with a number of ceramic

materials, including β-SiC, α-alumina, $MgAl_2O_4$ spinel, forsterite and borosilicate glasses, up to the temperature at which it decomposes under a pressure of 100 kPa (1 atm), i.e. $\approx 950\,°C$.

Beyond this limit and under a high enough pressure (to avoid the decomposition of the phyllosiloxide), interdiffusion phenomena occur between the ceramic material and the phyllosiloxide, which are more extended for α-alumina and forsterite than for spinel and β-SiC. However, at 1200 °C the reactivity of the phyllosiloxide with the ceramics becomes almost the same. Borosilicate glass ($80SiO_2$–$13B_2O_3$–$3.5Na_2O$) with a softening point lower than the decomposition onset of $KMg_2AlSi_4O_{12}$ at relatively low temperatures, appears to be an ideal matrix material in association with e.g. SiC fibres, for exploring the potential of the phyllosiloxide as an interphase in CMCs.

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