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

Part II *Coated fibres and model composites*

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

Nicalon fibres were coated with a sol–gel precursor of the $KMg_2AlSi_4O_{12}$ phyllosiloxide, by dip-coating. However, both the 1 μm gel coating and the fibres were severely damaged during the phyllosiloxide crystallization under supercritical conditions (700 °C, 50 MPa, 48 h) in glycol monomethyl ether. A 3–5 μm thick coating of $KMg_2AlSi_4O_{12}$ was successfully applied from a slurry on SiC chemical vapour deposited- or α-alumina single crystal-monofilaments, in which the phyllosiloxide platelets were oriented parallel to the fibre surface in a first approximation. Small one-dimensional model composites with a borosilicate matrix were prepared from these coated monofilaments, by hot pressing (900 °C, 30 MPa, 10 min). Evidence of fibre pull-out in bending failure tests suggesting a weak fibre matrix bonding, was observed. It is not known whether this weak bonding is related to the layered crystal structure or to the porosity of the phyllosiloxide interphase.

1. Introduction

Improving the oxidation resistance of ceramic matrix composites (CMCs) is a key issue with a view to using these materials in applications at high temperatures under oxidizing atmospheres (e.g. in jet engines). CMCs are tough materials when the fibre–matrix bonding is weak enough, which supposes the use of a fibre coating, referred to as the interphase, during processing. The most commonly used interphase materials, e.g. pyrocarbon (PyC) or turbostratic BN, display a layered crystal structure. When the weakly bonded layers are deposited parallel to the fibre surface, they favour the deflection of the matrix cracks formed under loading, from mode I to mode II (i.e. parallel to the fibre axis, the load being applied in the fibre direction), thus preventing the early failure of the fibres by the notch effect [1, 2]. Although both PyC and turbostratic BN are excellent mechanical fuses in terms of crack-deflection ability, they are sensitive to oxidation, the former beyond ≈500 °C and the latter beyond ≈850 °C.

There are very few refractory oxides exhibiting layered crystals structures consisting of weakly bonded layers, which could be used as interphase materials to replace PyC and turbostratic BN in composites designed for use in oxidizing atmospheres. Phyllosilicates such as phlogopite micas, $KMg_3(Si_3Al)O_{10}(OH)_2$, display layered crystal structures but their thermal stability is limited owing to a decomposition process involving the OH^- ions. Their decomposition can be shifted to higher temperatures but not suppressed, by replacing the OH^- ions by F^- ions, such as in fluorphlogopite mica, $KMg_3(Si_3Al)O_{10}F_2$. In fact, fluorphlogopite has been tentatively used as interphase in glass-ceramic matrix composites [3].

Recently, a new family of layered oxides, derived from the phyllosilicates but free of OH-ions, referred to as phyllosiloxides, has been designed on the basis of appropriate coupled anionic/cationic substitutions and prepared according to a sol–gel/solvothermal treatment process [4]. One of these phyllosiloxide derived from phlogopite, namely $K(Mg_2Al)Si_4O_{12}$, has been found stable enough at high temperatures under pressure, possibly to be used as an interphase in a fibre-reinforced borosilicate glass-matrix (known to exhibit a rather low softening point).

The aim of the present work, presented as two companion papers, was to try to demonstrate that such a phyllosiloxide could act as a mechanical fuse and could be used as an interphase. Part I was devoted to the study of the thermochemical compatibility of the phyllosiloxide with various fibre and matrix materials [5]. Part II deals with an attempt to coat fibres with the phyllosiloxide and to prepare

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model composites with these coated fibres and a borosilicate glass matrix.

2. Experimental procedure

2.1. Coated ceramic fibres

The $KMg_2AlSi_4O_{12}$ phyllosiloxide has been deposited on ceramic fibres according to two different coating processes and taking into account the two following requirements: (i) the coating must be crystallized as platelets (e.g. 1 μm in size) oriented parallel to the fibre surface [2], and (ii) the coating thickness should be thin enough (less than about 1 μm). The two deposition processes are dip-coating in a sol followed by a gelification step and a crystallization treatment under solvothermal conditions, on the one hand, and coating with a phyllosiloxide slurry and drying, on the other hand.

2.1.1. Dip-coating process

Si–C–O Nicalon fibres (Nicalon NL202 ceramic grade from Nippon Carbon, Japan), which have been desized by oxidation in air at 400–500 °C, were coated with a layer of phyllosiloxide, according to four-step process. In a first step, a sol precursor of $KMg_2AlSi_4O_{12}$ was prepared by dissolving the corresponding alkoxides in a solvent, glycol monomethyl at a concentration c. A polymeric plasticizer was added at a concentration c' in order to control the viscosity of the sol. In a second step, the sol was deposited on the fibre by dip-coating [6, 7]. The process simply consisted in dipping the fibre in the sol and then in pulling it out of the sol reservoir at a slow and constant speed. In a third step, the coated fibre was immediately heated in air at about 150 °C in order to vaporize the solvent and convert the sol to a gel. The dip-coating/sol–gel conversion was repeated several times up to the desired coating thickness. Finally, the coated fibre was submitted to a high temperature ($T = 700–750\,°C$) high pressure ($50 < P < 100$ MPa) treatment under solvothermal super-critical conditions (the solvent being that used for the sol), in order to crystallize the amorphous gel into $KMg_2AlSi_4O_{12}$ platelets, according to a procedure which has been depicted elsewhere [4].

2.1.2. Slurry-coating process

A phyllosiloxide slurry was prepared by dispersing a $KMg_2AlSi_4O_{12}$ powder (submicronic grain size) in a liquid consisting of a mixture of polyvinylic alcohol, water and acetone, under ultrasonic agitation conditions. The slurry with a concentration of phyllosiloxide close to 1–1.5 g ml^{-1}, remained stable over several days.

The slurry was applied to large-diameter monofilaments, namely SiC chemical vapour-deposited (CVD) monofilaments (SiC–CVD: Sigma monofilaments from B.P.) and α-alumina single-crystal fibre (Sapphire from "Saphikon"), 106 and 150 μm diameter, respectively. Such monofilaments were thought to be more appropriate for slurry coating than yarn fibres. The coating was achieved by immersing the monofilaments in the slurry and gently releasing the liquid by vaporization at ≈80 °C. Such conditions were expected to favour the deposition of the phyllosiloxide platelets preferentially parallel to the fibre surface.

2.2. Model one-dimensional composite

A model one-dimensional composite was prepared from a borosilicate glass (Pyrex borosilicate glass) powder (SiO_2 80 wt%; B_2O_3 13.1 wt%; Na_2O 3.5 wt%, as the main species) and SiC or α-Al_2O_3 large-diameter monofilaments coated with the phyllosiloxide, as depicted in Section 2.1. Lengths of coated monofilaments were set in a one-dimensional arrangement in a small cylindrical graphite die (inner diameter 15 mm), with the glass powder. Densification was achieved by hot-pressing. Temperature was raised with a heating ramp of 10 °C min^{-1}, up to 900 °C (a temperature at which the phyllosiloxide is still stable [4] and which is higher than the softening point of the glass). Pressure ($P = 30$ MPa) was applied unidirectionally beyond T_g (≈600 °C). The sample was then slowly cooled to room temperature.

Plane multilayers representative of the model composite, i.e. consisting of a disc of ceramic material (SiC or α-Al_2O_3), a layer of phyllosiloxide and a layer of borosilicate glass powder, were prepared with the same experimental procedure.

2.3. Characterization

The morphology of the coated fibres and that of the composite failure surface were observed with a scanning electron microscope (SEM, Jeol 840). The orientation of the phyllosiloxide platelets in the plane coatings was characterized by X-ray diffraction (XRD, Siemens D5000 diffractometer), according to the pole figure method. The atomic composition profiles across the interfaces were recorded either with X-ray electron probe micro-analyser (EPMA, CAMEBAX from CAMECA) or with an Auger electron spectroscopy (AES) microprobe (Physical Electronics 590, AES microprobe from Physical Electronics). The state of crystallization of the interphase was assessed by transmission electron microscopy (TEM, Jeol 2000 FX TEM).

3. Results and discussion

3.1. Coated fibres

The dip-coating parameters, namely, the concentrations of the sol in phyllosiloxide c and in plasticizer c', the viscosity of the sol and the pulling out speed, have been optimized on the basis of scanning electron micrographs (showing amongst others, the continuity of the deposit, its thickness, its adhesion to the substrate and the occurrence of cracks). The optimized parameters are given in Table I. Under such conditions, the amount of material deposited after one dip-coating/sol–gel conversion sequence on the fibre surface was too thin to be detected by SEM analysis. Five sequences were necessary to yield a 1 μm thick coating.

TABLE I Optimized values of the dip-coating process

Dip-coating parameters	Optimized values
c (g/100 ml)	1.3
c' (g/100 ml)	0.25
Sol viscosity (P)	2.2×10^{-2}
Pull-out speed (mm min^{-1})	25

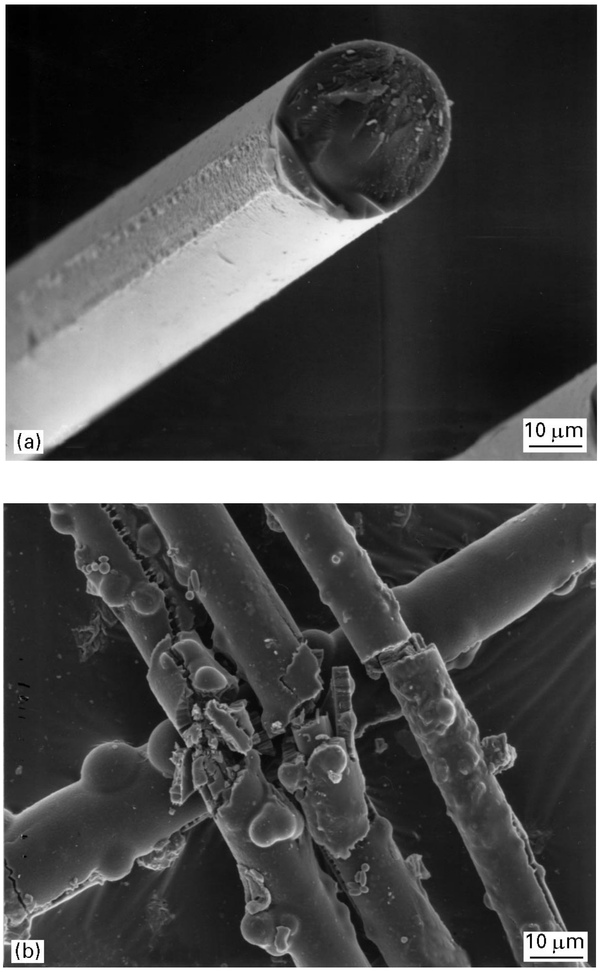

Figure 1 Scanning electron micrographs of Nicalon fibres coated according to the dip-coating process: (a) homogeneous 1 μm thick gel coating, (b) coated Nicalon fibres after the solvothermal treatment using glycol monomethyl ether as solvent, in supercritical conditions.

As shown in Fig. 1a, the gel coating is continuous, adherent to the fibre surface and crack-free. The thickness of the coating was also measured by laser interferometry (fibre diameter measured before and after coating), according to a technique which has been depicted elsewhere [8]. The data (13 ± 0.5 and 15 ± 0.5 μm, respectively) were consistent with a gel coating thickness of about 1 μm.

Under the solvothermal supercritical conditions reported to be necessary for crystallization of the gel as platelets with a 1 μm mean size [4], namely, $T = 750\,^{\circ}\mathrm{C}$, $P = 100$ MPa and $t = 48$ h, the coated Nicalon fibres were severely damaged, presumably as the result of interactions with the fluid under supercritical conditions. As shown in Fig. 1b, numerous cracks are observed along the fibres which have even been fragmented into small lengths. Additionally, nuclei have been formed at the fibre surface, and were identified as silica by AES-analysis. Lowering both temperature and pressure to 700 °C and 50 MPa, did not significantly change the results. Tentatively, the damage experienced by the coated Nicalon could be explained as follows: (i) a dissolution of the gel and partly of the Si–C–O fibres in the fluid under supercritical conditions, and (ii) a reprecipitation of the elements mainly as silica. These phenomena are relatively common in solvothermal reactions. In fact, they are even used to produce α-quartz single crystals [9]. Therefore, this coating route was temporarily abandoned (although the use of a more appropriate fluid could be envisaged).

As shown in Fig. 2a, a homogeneous crack-free coating of phyllosiloxide could be deposited on both SiC–CVD and α-alumina large-diameter monofilaments. Furthermore, a preferred orientation of the phyllosiloxide platelets is clearly apparent from the SEM image recorded at high magnification (Fig. 2b). The coating thickness was determined to be 3–5 μm on the basis of laser interferometry data.

The occurrence of a preferred orientation of the platelets parallel to the substrate surface was also

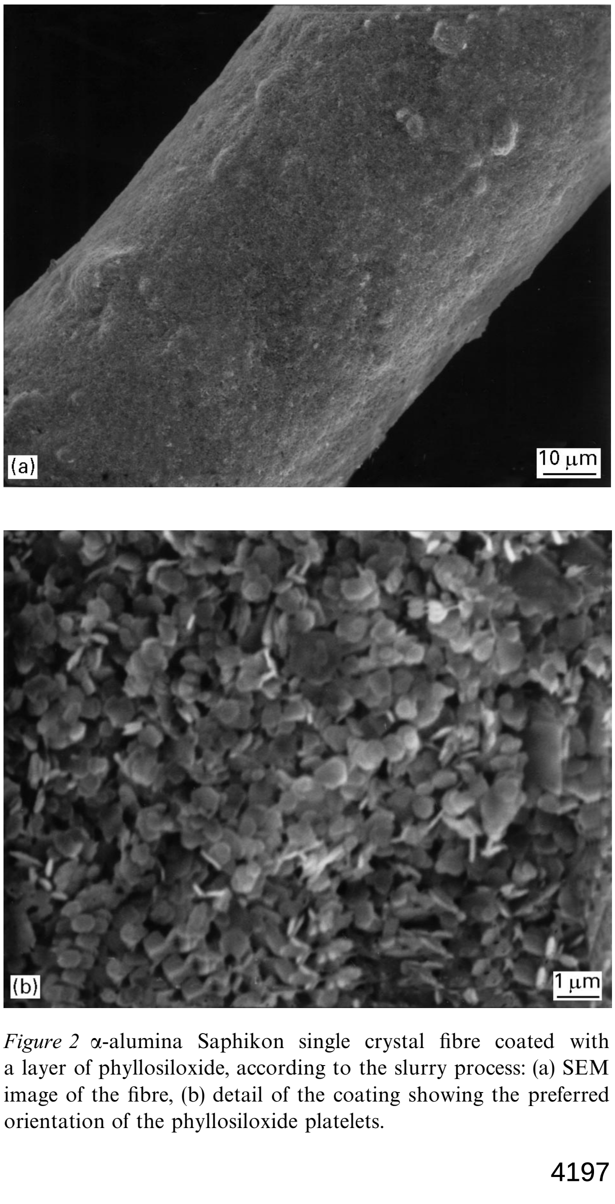

Figure 2 α-alumina Saphikon single crystal fibre coated with a layer of phyllosiloxide, according to the slurry process: (a) SEM image of the fibre, (b) detail of the coating showing the preferred orientation of the phyllosiloxide platelets.

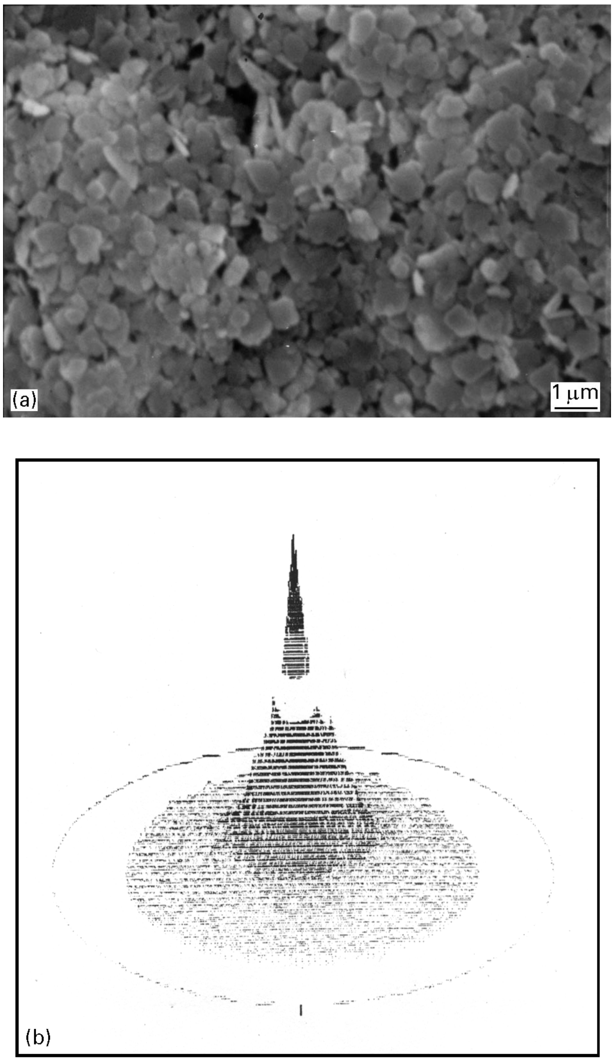

Figure 3 Preferred orientation of the phyllosiloxide platelets deposited on a plane disc of α-alumina from a slurry as assessed from (a) an SEM image, and (b) an XRD (0 0 6) pole figure.

observed in layers of phyllosiloxide deposited on plane discs (15 mm diameter) of α-alumina from the same slurry and according to the same experimental procedure. This preferred orientation is clearly apparent from the SEM-image (Fig. 3a) and the 0 0 6 pole figure (Fig. 3b). Thus, and as could be expected from their morphology, the phyllosiloxide platelets have a tendency to lie flat on the substrate (the surface of the large SiC or α-alumina monofilaments or that of a plane α-alumina disc) when the liquid of the slurry is progressively removed by gentle vaporization. Additionally, the slurry-coating process did not damage the reinforcement because it is performed at low temperature in a non-aggressive liquid medium.

3.2. Model composites

Within the scope of the present preliminary study, the main objective was to establish whether (i) a thin layer of oriented phyllosiloxide platelets could effectively act as a mechanical fuse, and (ii) there was any interdiffusion between the interphase and a borosilicate matrix during processing. The study has been conducted on two model materials: one-dimensional composites with SiC–CVD, or α-alumina monofilaments and the corresponding multilayer materials with planar interfaces.

As shown in Fig. 4, some fibre pull-out indicative of a weak fibre/matrix bonding is apparent from the

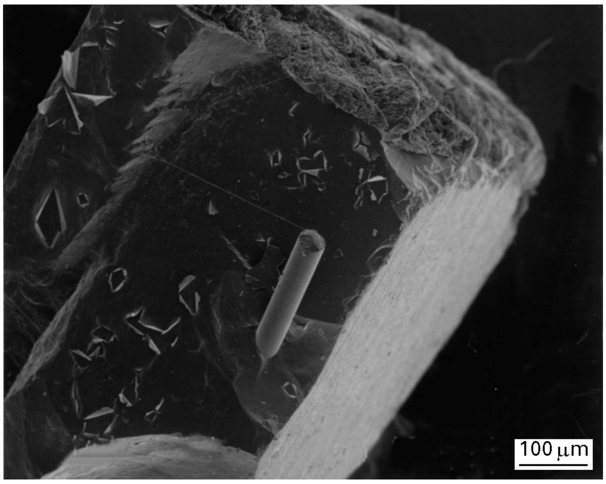

Figure 4 Bending failure surface of an α-alumina (Saphikon)/phyllosiloxide/borosilicate glass matrix composite showing some evidence of fibre pull-out.

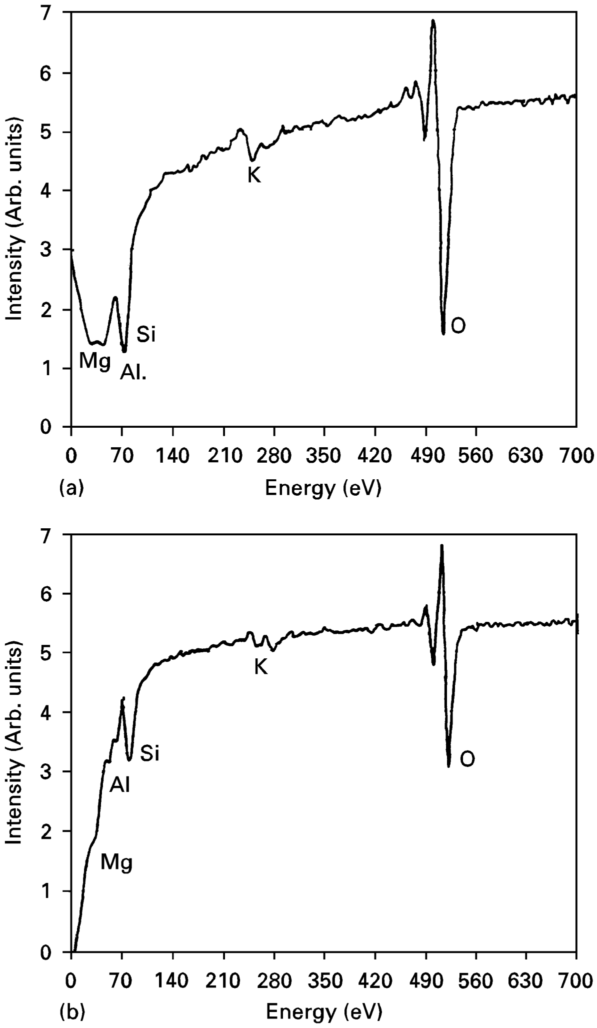

Figure 5 Auger electron spectra recorded from the failure surfaces of the model composite shown in Fig. 4: (a) from the surface of a pulled-our α-alumina fibre, and (b) from the corresponding trough in the borosilicate matrix.

bonding failure surface of an α-alumina (Saphikon)/phyllosiloxide/borosilicate one-dimensional composite. Furthermore, the AES-spectra recorded from the surface of the pulled out fibre (Fig. 5a) and from the corresponding trough in the borosilicate matrix (Fig. 5b) suggest that failure may have occurred within the phyllosiloxide layer itself because its constitutive elements are present on both sides. Conversely, attempts made to prepare a thin foil for TEM analysis, have failed. Tentatively, the phyllosiloxide layer may have been too weak or not sintered enough to experience without damage the ion-etching thinning procedure. Finally, EPMA line profiles showing the variations of the elemental composition across the fibre/matrix interfacial zone were recorded for the composites with SiC-CVD or α-Al_2O_3 monofilaments (Fig. 6). They show the occurrence of the phyllosiloxide interphase between the fibre and the matrix. The related interfaces on both sides of the interphase are broad, each of them extending over about 2 μm. This feature could be explained by some interdiffusion (however, the duration of hot pressing at 900 °C was only 10 min) and/or by the fact that the EPMA line profiles have not been deconvoluted.

Complementary information was obtained from the TEM analysis of a thin foil cut perpendicular to the planar interfaces of the α-Al_2O_3/phyllosiloxide/borosilicate multilayer. HR-TEM images have confirmed that the phyllosiloxide is still present near the α-alumina/interphase interface. Conversely, the interphase material appeared amorphous near the interphase/matrix interface. These data suggest that some interdiffusion may have occurred between the borosilicate glass and phyllosiloxide layers during processing. It could have been enhanced by some infiltration of the borosilicate glass in the phyllosiloxide layer by viscous flow during the hot-pressing step. At 900 °C, the phyllosiloxide does not undergo sintering and is assumed to remain porous. The infiltration of this porous medium by the borosilicate glassy phase, together with some reaction between the phyllosiloxide and the borosilicate, may explain the amorphous character of the interphase near its interface with the glass. Finally, it is noteworthy that a SiC-diffusion barrier has been recently used to prevent interdiffusion phenomena in Nicalon/BN/SiC/BMAS composites. In the dual BN/SiC interphase, the BN sublayer acts as a mechanical fuse, whereas the SiC sublayer impedes interdiffusion between the glass-ceramic matrix and BN [10].

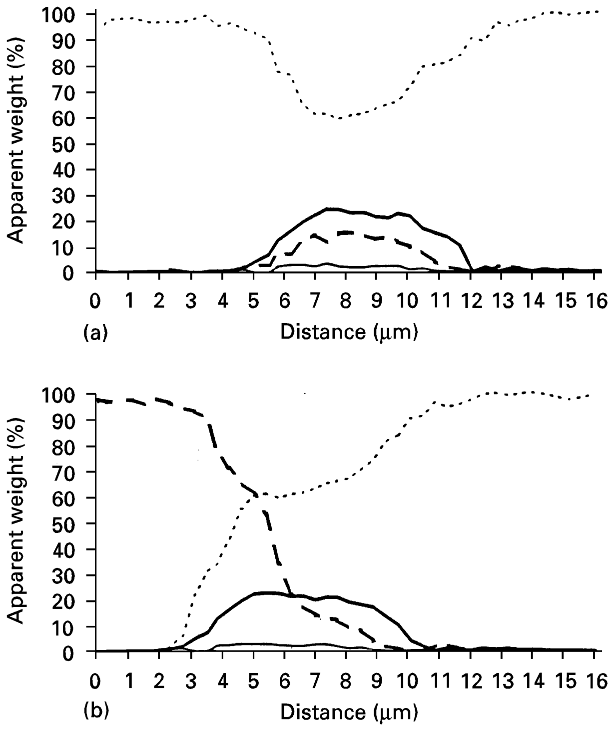

Figure 6 EPMA line profiles across the fibre–matrix interfacial zone in one-dimensional composites with phyllosiloxide interphases, a borosilicate glass matrix and (a) SiC-CVD (Sigma) monofilaments, (b) α-alumina (Saphikon) single-crystal monofilaments (the B_2O_3 data are not shown and carbon was not analysed in (a)). (- - -) SiO_2, (———) MgO, (— —) Al_2O_3, (——) K_2O.

4. Conclusion

1. Si–C-based fibres have been successfully coated with the sol–gel precursor of the phyllosiloxide $KMg_2AlSi_4O_{12}$ according to a dip-coating process. However, the coating and even the fibre itself were severely damaged during the crystallization of the gel under supercritical conditions in glycol monomethyl ether fluid.

2. A coating of $KMg_2AlSi_4O_{12}$ was applied from a slurry on SiC–CVD and α-alumina large-diameter monofilaments. The phyllosiloxide platelets are preferentially oriented parallel to the fibre surface.

3. Model one-dimensional composites were obtained by hot pressing these coated monofilaments within a borosilicate matrix at 900 °C. After failure in bending, some evidence of weak fibre bonding and fibre pull-out was observed, debonding occurring apparently in the phyllosiloxide interphase. However, it is still uncertain whether this easy debonding is related to the layered structure of the phyllosiloxide or to the porosity of the interphase.

4. Some interdiffusion may have occurred between the phyllosiloxide and the borosilicate glass during processing, partly enhanced by viscous flow of the glass in the porous interphase.

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