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Oxide CMCs: interphase synthesis and novel fibre development

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Abstract

Strategies which have been used in the synthesis of high temperature interphases with debond capability in oxide/oxide systems have been: (i) the formation of layered oxides (β-aluminas or magnetoplumbites) with preferred crystal orientation due to in-situ interface reactions between phases deposited from vapour or liquid precursors and (ii) the deposition on fibre surfaces of complex oxides (vanadates and phosphates, principally of the rare earths) from colloidal precursors or by magnetron sputtering. This paper is primarily concerned with the latter. The constitution and thermal stability of these interphases has been studied with reference to potential fibres and matrices (alumina, YAG and mullite). Included within the program are newly developed single phase mullite fibres and examples of these are also presented. © 2000 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Oxide/oxide CMCs are being developed in an effort to overcome the limit of application temperature reached by most experimental non-oxide CMCs as a result of their oxidative instability. The trend towards an all oxide CMC has seen the development of a range of oxide fibres with early examples being those based largely on Al_2O_3. More recently, the commercially available "Nextel^{TM}" series of fibres produced by 3M has received much attention. These fibres are composed of Al_2O_3 with varying amounts of SiO_2 for grain size control and the promotion of mullite crystallisation for improved creep resistance and stress-rupture properties. It is known, however, that these fibres reach a temperature limit of application due to a phase instability at around 1200°C and a subsequent degradation of mechanical properties. Part of this research program and related projects involves the development of fibres based on mullite and YAG, oxides both known for their creep resistance.

Crucial to the development of an oxide/oxide CMC is the selection of a suitable interface material which will be thermally and chemically stable with both the fibre and the matrix as well as exhibiting the desired de-bond characteristics. An optimised interface microstructure is based on the micromechanical parameters τ and G_i which represent the shear stress in the interface and its de-bond energy, respectively. The interphase zone should act as a reaction barrier between fibre and matrix, inhibit diffusion of atmospheric species to the fibres and remain intrinsically stable at high temperatures in differing atmospheres, e.g. to avoid channelled oxidation from exposed fibre ends or via matrix microcracks.

Strategies which are being used for oxide/oxide systems have attempted to replicate some of the microstructural features of the non-oxides using phases with a low-cohesion 'layer-plane' by 'in-situ' reaction between a simple fibre coating and surrounding matrix, e.g. a cerium-doped zirconia layer applied to the fibre surface reacting with an alumina matrix to produce oriented crystals of Ce-doped $\beta\ Al_2O_3\ (Ce_2O_3.11\ Al_2O_3)$[1]. The preferred orientation, with β-alumina layer plane tangential to the filament surface, favours interfacial debond and is an improvement on similar (La-β alumina) interphases formed by liquid-precursor deposition. However, debond shear stresses in filament "push-through" tests are relatively high even though subsequent sliding stresses ($\tau \sim 40$–50 MPa) are within reasonable limits for damage-tolerance.

A second strategy is an empirical search for complex oxides which have a high probability of low cohesion with matrix or fibre due to polarisation of oxygen bonds by high valence cations. These are exemplified by vanadates, phosphates or niobates, having the generic formula $MX0_4$, where X is the pentavalent cation, tetrahedrally or octahedrally co-ordinated by oxygen, and M is a rare earth or ytrrium ion in 8- or 9-fold co-ordination with oxygen.

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Table 1
Summary of crystal structures and known melting points (T_m) of selected MXO_4 compounds

	Phosphate	Vanadate	Niobate
La	Monoclinic (monazite) $T_m = 2072°C$	Monoclinic (monazite) T_m	Monoclinic (fergusonite) $T_m = 1620°C$
Nd	Monoclinic (monazite) $T_m = 1975°C$	Tetragonal (zircon) $T_m > 1500°C$	Monoclinic (fergusonite) $T_m > 1000°C$
Y	Monoclinic/hexagonal $T_m = 2000°C$	Tetragonal (zircon) $T_m = 1810°C$	Monoclinic (fergusonite) $T_m = 2000°C$

Recent research[2–5] has used the second strategy, and examples of potential "interphase" oxides which have been studied in current UK and EC projects are covered in this paper, including their thermal and chemical stability with selected oxides and the evaluation of various methods of deposition of the interphases onto commercially available woven oxide fibres.

1.1. MXO_4 type interphases

In general, these compounds have related structures (xenotime, monazite, fergusonite) and exhibit high temperature congruent melting. Those selected for study here are summarised in Table 1. With the exception of $NdVO_4$ and $NdNbO_4$, these compounds have been compared in relation to the ease of stoichiometric synthesis, deposition method, reactivity and debond-energy with candidate oxides for CMC fibre and matrix phases, namely Al_2O_3, mullite and YAG.

This selection encompasses alternative M and X chemistries which are known to exist with the monazite structure and allows comparison of compounds with the same X but different structure-type with differing M. Such a comparison might enable the critical parameters for variable debond condition to be identified. For example, within the vanadate and phosphate series, the crystal structure changes from monazite (monoclinic) to xenotime (tetragonal-zircon iso-structure) with changing M in the rare earth series. An additional selection factor is based on thermal stability and most compounds melt congruently at temperatures above 1600°C.

It is important to consider the ease of synthesis and tolerance of compositional deviations from the exact 1:1 ratio of M_2O_3:X_2O_5 in each binary system. For example, in earlier work, an apparent reactivity between Al_2O_3 and $LaPO_4$ was later shown to result from liquid formation above 1050°C in P_2O_5 rich compositions, consistent with a peritectic isotherm in this system.[2] In the Nd_2O_3–P_2O_5 system, however, the isotherm in P_2O_5-rich $NdPO_4$ compositions is at 1270°C and hence $NdPO_4$ is a favoured interphase material. In addition, Nd_2O_3 is less hygroscopic than La_2O_3 and, as a more readily handled precursor, facilitates better control over the composition of the resultant interphase.

1.2. Physical vapour deposition (PVD) of interphases

Although there are many different ways of depositing an interphase coating onto a ceramic fibre, the method investigated here is that of physical vapour deposition. Deposition from the liquid phase (sol) has also been studied and reported previously for infiltration of Nextel 720 satin weave with a $NdPO_4$ interphase.[6] The liquid phase deposition approach was adopted based on the need to enable scale up of the infiltration process in order to meet the requirements of real component fabrication using CMCs, where coating of fabric layers rather than individual fibres or fibre tows is desired. PVD, however, offers the advantage of being able to achieve a more uniform coating together with potentially better control of the layer thickness and composition.

2. Experimental procedure

Reaction couples were prepared by mixing single crystal filaments (Saphikon) or substrate fragments (YAG) with the MXO_4 powders. The mullite source is a commercial sol. The mixtures were then isostatically pressed and co-sintered at 1400°C for up to 8 h. The MXO_4 powders were synthesised from liquid precursors or by hydrolysis of colloidal mixtures of the consituent oxides.[7,8]

Compatibility is characterised by interfacial cross diffusion or the appearance of additional phases, detected by X-ray diffraction, electron microscopy and interfacial microprobe analysis of polished and fracture surfaces.

PVD was carried out via RF magnetron sputtering in argon. Targets were prepared by spin-coating substrates with alcoholic slurries of the interphase powders used in the reactivity studies, with the aid of binders and dispersants, followed by careful drying at room temperature and heat-treatment at 800°C for 2 h. The samples and targets were outgassed in the sputtering chamber for 24 h before each run.

New fibres presented in this work were sol-spun from inexpensive precursors.[1]

3. Results and discussion

Of the interphases shown in Table 1 ($NdVO_4$ and $NdNbO_4$ not studied), those considered compatible with

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[1] Morgan Materials Technology Ltd. Stourport-on Severn, Worcs., UK.

each of the candidate fibre/matrix oxides, after co-sintering at 1400°C, are shown in Table 2. An example of a non-reactive interface is that of $Al_2O_3/LaVO_4$ and Fig. 1. shows a typical interface exposed in a fracture surface. It can be seen that the only interactive features on the Saphikon debond surface are small ridges formed by grain boundary/interface energy equilibration during sintering.

In the other cases, one or more reaction products can be detected, for example, YVO_4 and YPO_4 in conjunction with Al_2O_3 both result in the appearance of a reaction layer at the interface, thought to be YAG and possibly with some substitution by the V^{5+} or P^{5+} ions. The niobates, whilst shown to be stable in contact with alumina and mullite, exhibited reactions with YAG resulting in the appearance of Al_2O_3 as well as at least one other phase. Another example is the compatibility of $LaVO_4$ with Al_2O_3 but a reactivity with YAG such that the YVO_4 interphase is favoured. Consequently, candidate interphases for some diphasic fibres or matrices (e.g. Al_2O_3/YAG) are not always identifiable.

Some caution is required, however, in using these model reaction couples since in real fabrication of CMCs, fibres or matrices may not be pure single or diphasic ceramics but contain residual grain boundary liquids or segregates. For example, some reaction has been identified for vanadates and niobates with Nextel 720 fibres (which have mullite/Al_2O_3 microcrystalline structures) whereas no reaction is detected with the separate phases (Table 2). This in part might be attributable to a known time-dependent microstructural instability exhibited by the Nextel 720 fibres, associated with a change from metastable pseudo-tetragonal $2Al_2O_3.SiO_2$ mullite to the orthorhombic 3:2 form via Al_2O_3 precipitation and shown by the XRD data in Fig. 2.[9] This instability becomes apparent at a temperature of 1200°C and, therefore, is expected to influence the performance of the interphases studied at a higher temperature in this work.

Table 2
Interphases considered compatible with selected oxides at 1400°C

Al_2O_3		YAG	Mullite
$LaPO_4$	$LaNbO_4$	YVO_4	No reactive couples detected
$NdPO_4$	$YNbO_4$	YPO_4	
$LaVO_4$			

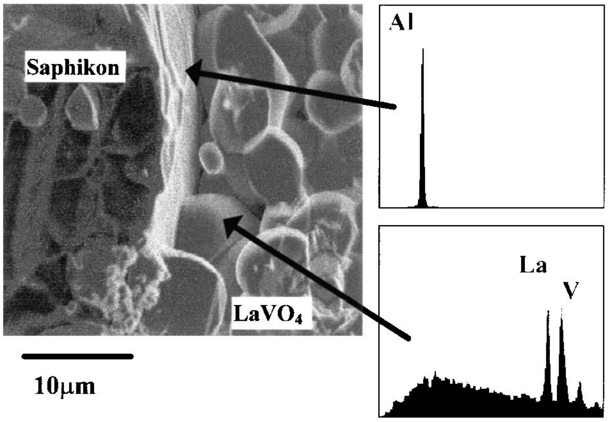

Fig. 1. $LaVO_4$ debond interface with Saphikon and EDAX analysis either side of interface.

RF magnetron sputtering of vanadates and phosphates has led to the preparation of fine grained, uniform coatings on oxide fibres and flat substrates. Compositional and phase analysis of thin films via EDAX and XRD show that stoichiometric transfer of the constituent ions is possible, resulting in the formation of an amorphous layer. This can be crystallised upon heating to around 800°C or above in air to yield the MXO_4 type compounds as characterised, for the example of $LaVO_4$ on Al_2O_3, by the XRD traces shown in Fig. 3. An example of a vanadate coating on FP Al_2O_3 fibres[2] is shown in the SEM micrograph in Fig. 4, where it can be seen that even though the surface of these particular fibres is relatively rough a complete coating can be achieved using the PVD technique. The TEM micrograph in Fig. 5. shows the layer to be

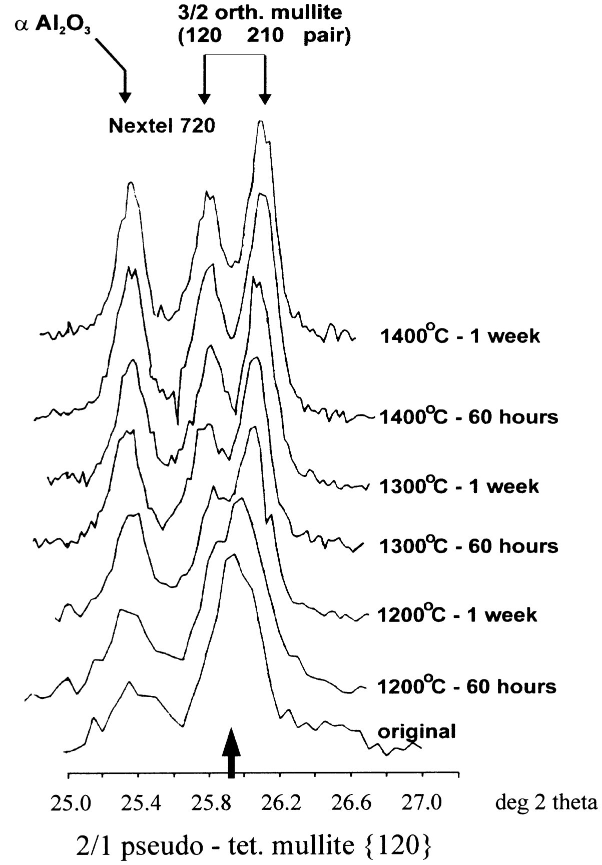

Fig. 2. XRD data depicting the microstructural instability of Nextel 720 fibres at 1200°C.

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[2] Du Pont Ltd. Hemel Hempstead, UK.

amorphous in the as-deposited form and highlights the surface roughness of these fibres.

During higher temperature annealing of the thin film interphases on oxide substrates the continous nature of the as-deposited films is lost and the coatings begin to form "islands", as can be seen in Fig. 6. Whilst it is recognised that there are a number of factors affecting the stability of a coating against break-up, including a critical grain size to film thickness ratio, this tendency of the coating to minimise its interfacial area might also be an indication of a propensity for debond if this is a consequence of a relatively high interfacial energy.

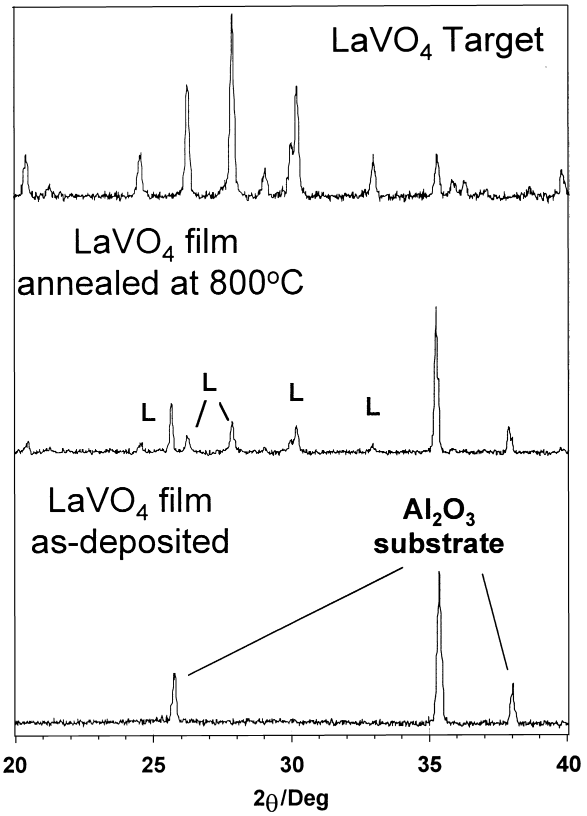


Fig. 3. XRD data showing development of monoclinic $LaVO_4$ phase (peaks labelled L) after annealing of amorphous sputtered films.

Fig. 5. TEM image of amorphous $LaVO_4$ PVD coating as-deposited on FP (Du Pont)-Al_2O_3 fibre.

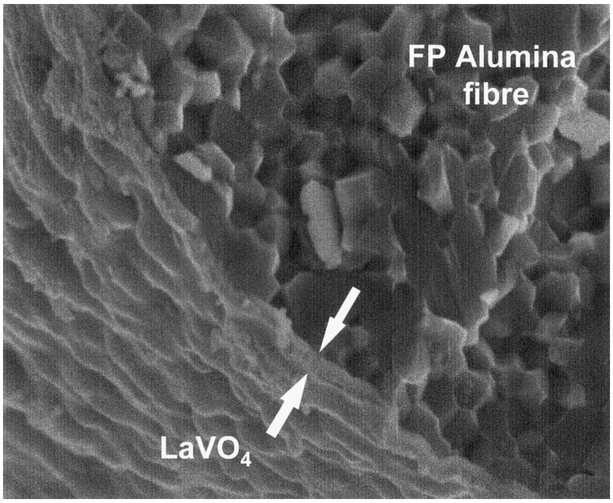


Fig. 4. SEM micrograph of PVD $LaVO_4$ coating on FP (Du Pont)-Al_2O_3 fibre.

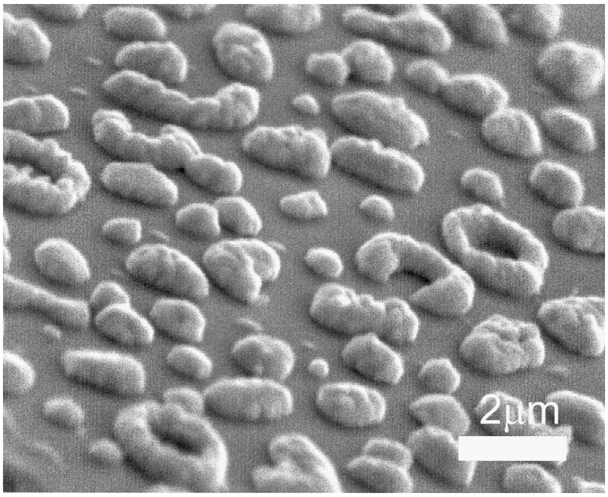


Fig. 6. SEM image showing "island" formation of $LaVO_4$ thin film on Saphikon after annealing at 850°C.

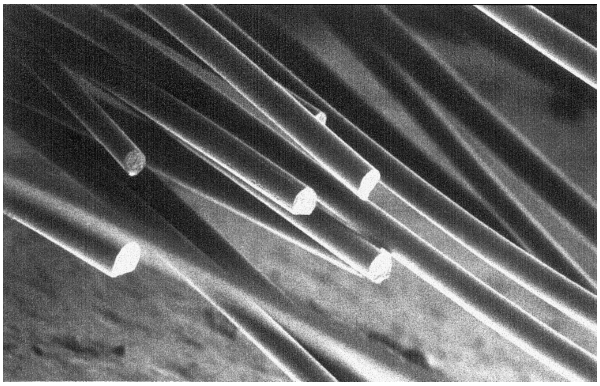


Fig. 7. Mullite sol-gel fibres, fired at 1400°C.

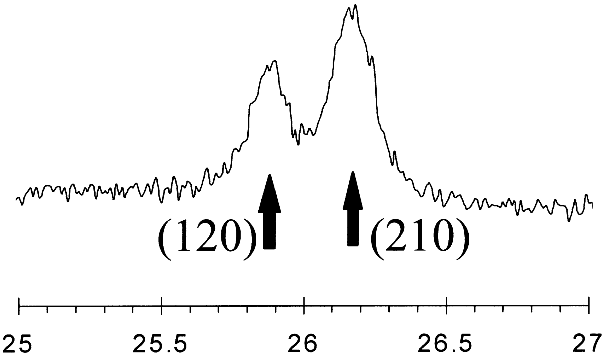


Fig. 8. XRD trace obtained from new mullite fibres, showing appearance of (120) and (210) pair of peaks characteristic of orthorhombic mullite.

An example of the new mullite fibres, with diameters approaching 10 μm and possessing a smooth, uniform surface is shown Fig. 7. EDAX analysis of these fibres shows a near theoretical 3:2 Al_2O_3:SiO_2 composition and XRD shows that complete crystallisation to the orthorhombic phase occurs after firing at around 1300°C, characterised by the splitting of the {120} mullite peaks into the (120) and (210) pair, as depicted in Fig. 8. TEM examination of early fibres showed the presence of nano-sized intragranular pores after firing (see Fig. 9), but the use of a sintering additive has eliminated this porosity to yield a fibre microstructure of equiaxed, contiguous grains with negligible amounts of intergranular residues, as shown in Fig. 10.

Initial mechanical properties measurements of the new mullite fibres are encouraging, with tensile strengths in excess of 2GPa being achieved. A comparison of the m ratio in bend stress relaxation tests,[10] shown in Fig. 11, also shows the creep properties of these fibres to be superior to the Nextel 720 fibres at 1200°C and similar to those reported for directionally solidified and edge-defined film growth YAG/Al_2O_3 fibres.[11] Values of $m = 0.51$ and 0.64 were measured for the fibres after firing at 1200°C and 1400°C, respectively, compared with $m = 0.29$ for the Nextel 720 fibres.

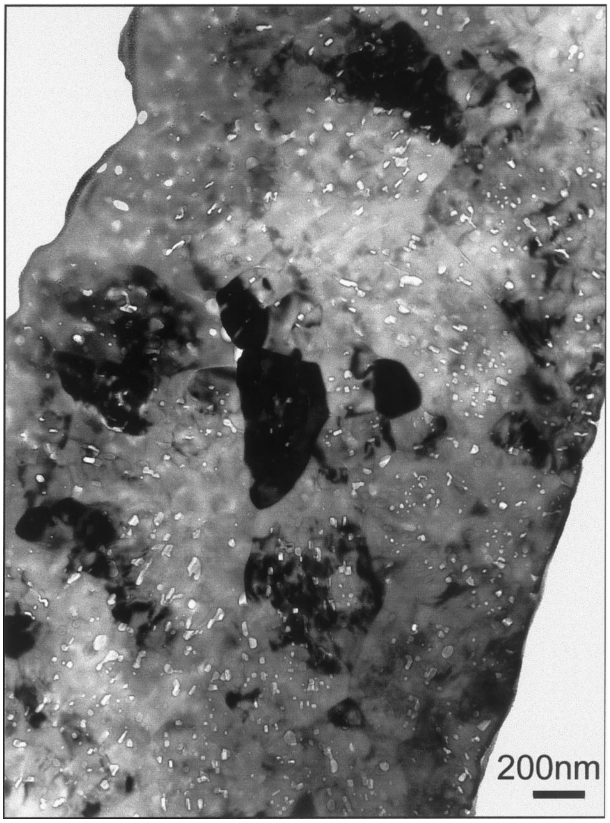


Fig. 9. TEM image showing intragranular micro-porosity present in first generation sol–gel mullite fibres.

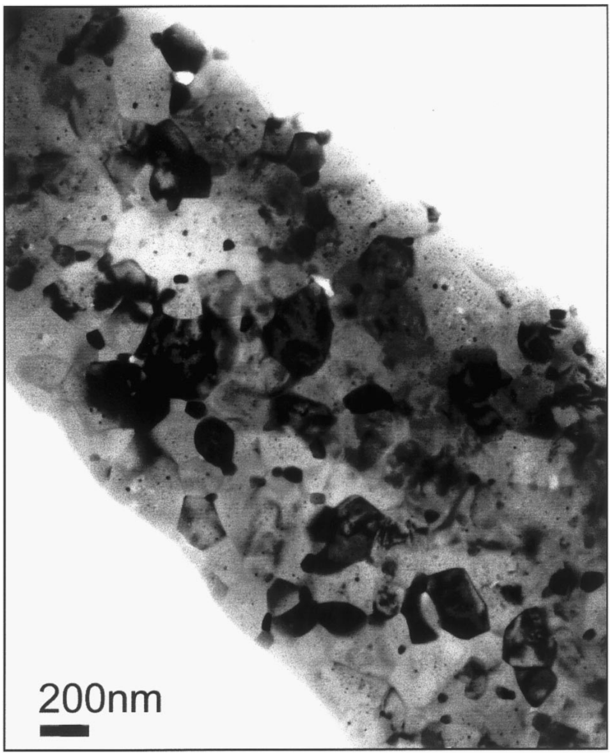


Fig. 10. TEM image showing absence of intragranular micro-pores and contiguous, equiaxed grains in new sol–gel mullite fibres prepared using a sintering additive and fired at 1400°C.

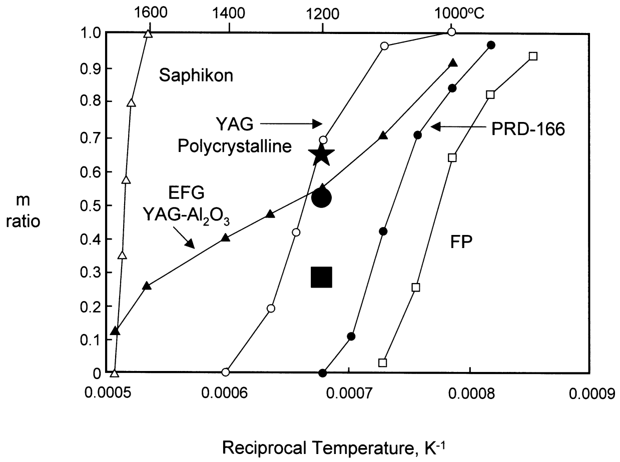
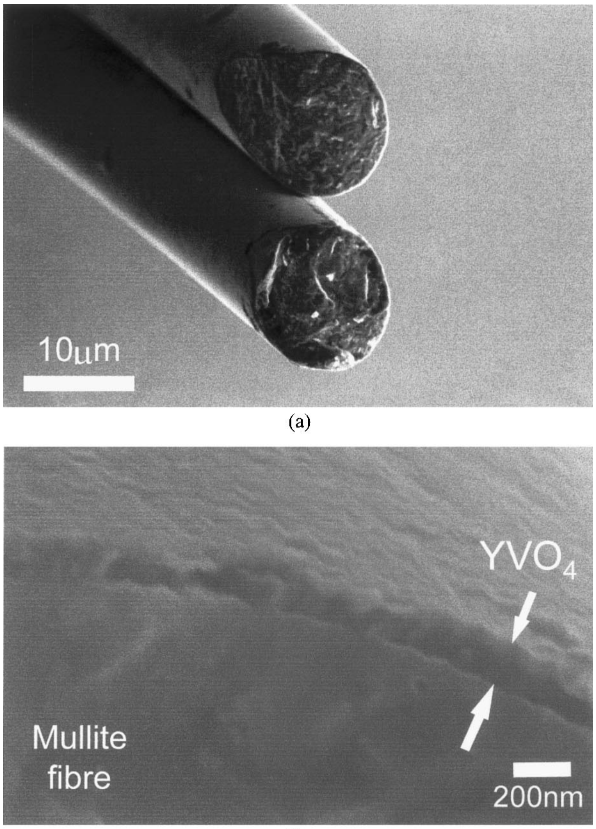


Fig. 11. Bend stress relaxation data for the new sol–gel mullite fibres tested at 1200°C after firing at 1200°C (●) and 1400°C (⋆), compared with Nextel 720 (■) and other oxide fibres (adapted from Ref. 11).



(a)

(b)

Fig. 12. SEM images: (a) showing new mullite fibres with YVO$_4$ PVD coating and (b) the appearance of the interphase/fibre interface at higher magnification.

The new mullite fibres are currently being studied in relation to reactivity and debond issues with the MXO$_4$ interphases for CMC applications. An example of these fibres with an as-deposited, sub-micron, yttrium vanadate PVD coating can be seen in the SEM micrograph in Fig. 12.

4. Conclusions

Lanthanum vanadate, yttrium vanadate and neodymium phosphate have been shown to be stable interphases with at least one of the candidate oxides for CMC fabrication considered in this work, i.e. alumina, YAG or mullite. Their phase compatibility at temperatures up to 1400°C for several hours is an indication that these compounds might offer an alternative to lanthanum phosphate previously reported as a suitable interphase for oxide-oxide CMCs.

These novel interphases have been successfully deposited by PVD via RF-magnetron sputtering onto a number of commercially available and newly developed oxide fibres as well as onto flat substrates to yield uniform coatings.

It remains to be seen whether these compounds will exhibit the desired debonding behavior required of a successful CMC interphase. Further work is underway to investigate this and to elicit further information about the exact nature of the interfaces, e.g. preferred orientation, between these vanadates and phosphates and the oxides likely to be used as CMC fibres/matrices.

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