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Temperature-induced fibre/matrix interactions in porous alumino silicate ceramic matrix composites

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Abstract

The thermal stability of alumino-silicate fibre (Nextel 720)/porous mullite matrix composites was investigated in the temperature range between 1300 and 1600°C. In the as-prepared state the fibres consist of mullite plus α-Al_2O_3, while the porous mullite matrix includes minor amounts of a SiO_2-rich glass phase. Temperature-controlled reactions between the silica-rich glass phase of the matrix and α-Al_2O_3 at the rims of the fibres to form mullite have been observed. At the end of this process, virtually all glass phase of the matrix is consumed. Simultaneously, alumina-free layers about 1 μm thick are formed at the periphery of the fibres. The mullite forming process is initiated above about 1500°C under short time heat-treatment conditions (2 h) and at much lower temperature (1300°C) under long-term annealing (1000 h). Subsequent to annealing below the thermal threshold, the composite is damage tolerant and only minor strength degradation occurs. Higher annealing temperatures, however, drastically reduce damage tolerance of the composites, caused by reaction-induced gradually increasing fibre/matrix bonding. According to this study, the thermal stability of alumino silicate (Nextel 720) fibre/mullite matrix composites ranges between 1500°C in short-term and 1300°C in long-term heat-treatment conditions.

Keywords: Aluminosilicate fibres; Composites; Mullite; Reaction path; Thermal stability

1. Introduction

Oxide ceramics have a high potential for long-term high-temperature applications such as thermal protection systems in combustion chambers of gas turbine engines. Monolithic ceramics, however, are not suitable for many applications due to their inherent brittleness. A promising way to achieve tough and damage-tolerant ceramics is the reinforcement of ceramic bodies by ceramic long fibres.[1] Long fibre reinforced composites may exhibit non-brittle fracture behavior if the bonding between fibres and the matrix is relatively weak so that crack deflection and fibre pull-out do occur.[2] Weak fibre/matrix bonding is controlled by weak fibre/matrix interfaces, e.g. by low-toughness fibre coatings,[3] porous fibre coatings, or by "fugitive layers".[4] The homogeneous coating of fibres, however, is an expensive process, especially if chemical vapor deposition (CVD) techniques are taken into account. Moreover, suitable fibre coating materials such as turbostratic BN or C are not stable in air at high temperatures. An alternative approach for damage-tolerant all-oxide ceramic matrix composites was reported by Lange, Evans and coworkers.[5–7] This material which has been designated as "ceramic wood" consists of ceramic fibres embedded in a matrix of high porosity. The concept makes use of the porous matrix as a surrogate of a porous fibre/matrix interphase and was demonstrated succesfully for ceramic matrix composites consisting of alumina fibres and a matrix of Si_3N_4 or mullite.[5–7]

Ceramic matrix composites consisting of highly porous mullite matrices and alumino silicate fibres (3M, Nextel 720) recently have been fabricated by pressureless sintering of mullite-infiltrated fibre bundles in the Institute of Materials Research of the German Aerospace Center (DLR). To prevent fibre degradation during processing, the sintering temperature of the composite was not allowed to exceed 1300°C. Sintering activity of mullite precursors with stoichometric composition (72 wt% Al_2O_3, 28 wt.% SiO_2), however, is low in case of pressureless firing at 1300 °C. Thus, a mullite precursor slightly supersaturated in SiO_2 with respect to

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mullite was employed (68 wt.% Al_2O_3) though some glassy phase had to be accepted in the resulting mullite matrix. The porous mullite matrix composite shows quasi-ductile fracture behaviour and strength values of more than 300 MPa in case of unidirectional reinforcement with a fibre content of $\approx$45 vol.%.[8,9] Since the fibre strength after 1300°C heat treatment is $>$1500 MPa,[17] the maximum strength of the composite is significantly smaller than one would expect using the rule of mixture. Therefore, the strength of the composite seems to be controlled by fibre/matrix debonding processes rather than by direct fibre strength. Although the matrix contains more than 5% glassy phase, there is no excessive creep deformation of the composite at elevated temperatures. Preliminary investigations show that the creep behavior of the composites is controlled by the creep resistivity of the fibres rather than by matrix properties. Similar results recently were reported by Deng investigating SiC-fibre/mullite matrix composites.[10]

The aim of the present study is the investigation of thermally induced reactions between the silica-rich matrix and alumina-rich Nextel 720 fibres.[†] Reactions between SiO_2 (in the matrix) and α-Al_2O_3 (in the fibres) can be expected according to the Al_2O_3–SiO_2 phase diagram when the thermal activation of the samples is sufficient. The reactions between fibres and matrix have implications for the mechanical properties of the composite, which will be discussed in detail.

2. Experimental

2.1. Materials processing

Green bodies of the porous mullite matrix composites were fabricated by infiltration of fibre bundles with an aqueous mullite precursor (Siral, Condea, Germany) slurry and subsequent winding up on a mandrel. The infiltrated fibre tapes were removed from the mandrel in the moist stage, rolled in flat tapes, and sintered pressureless in air at 1300°C (60 min). The fibre content of the 1D-composite is approx. 45 vol.%. Details of the CMC processing are published elsewhere.[8] CMC samples were heat-treated at 1300°C (1000 h) and at 1400, 1500 and 1600°C (2 h) in air.

2.2. Characterization

The microstructural development was monitored by means of scanning electron microscopy (SEM) on polished sections. Due to the high matrix porosity, the samples were infiltrated with a low-viscous epoxy resin before grinding and polishing. SEM was performed using a LEO Gemini 982 microscope equipped with a field emission cathode and an Oxford EDX system. The Al_2O_3/SiO_2 ratio of matrix mullite crystals was determined via lattice constant data[11] using fibre-free model samples. Lattice constants were obtained from careful X-ray diffraction (XRD) measurements using a Siemens D 5000 XRD machine. In selected specimens, the composition of the submicron-sized matrix mullite crystals was checked by EDX in combination with a transmission electron microscope (Philips EM 430 equipped with a Tracor EDX system).

Three-point bending tests (40 mm span) were performed on 50×5×1 mm bars cut out of the 1D-composite material. At least eight specimens were tested for each firing series.

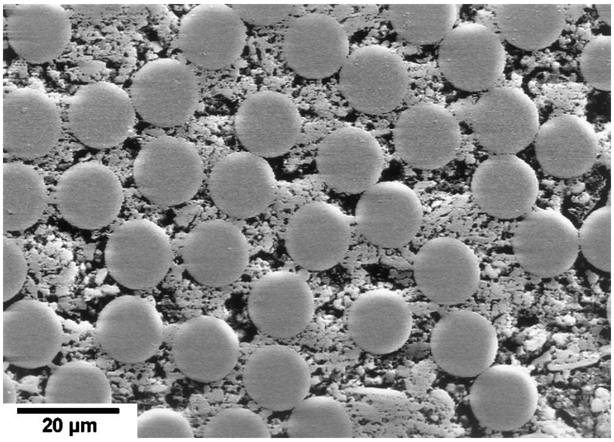

Fig. 1. Overview of the as-prepared alumino silicate fibre/porous mullite matrix composite (scanning electron micrograph from polished cross-section).

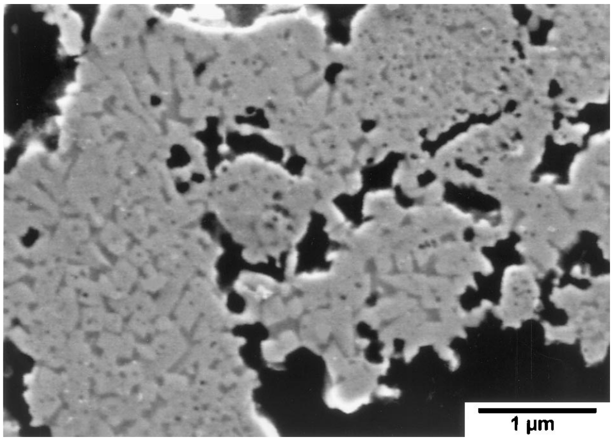

Fig. 2. Detail of the as-prepared alumino silicate fibre/porous mullite matrix composite. Note the high-porous mullite matrix with small glassy pockets existing between the rectangular mullite crystals.

[†] The composition of 3M Nextel 720 fibre is 85 wt.% Al_2O_3, 15 wt.% SiO_2. The fibre consists of α-Al_2O_3 plus mullite.

3. Results

Fig. 1 gives an overview of the as-prepared Nextel 720 alumino silicate fibre/porous mullite matrix composite. Fig. 2 shows the mullite matrix in higher magnification: it clearly demonstrates a very high porosity (≈50 vol.%) of the matrix. Moreover, small glassy pockets become visible between the mullite crystals. Microstructural details of heat-treated samples are given in Fig. 3 and 4. With increasing temperature, gradual coarsening of the fibre compounds, α-Al_2O_3 and mullite, occurs. Beside coarsening, dissapearance of α-Al_2O_3 in the fibre rim area can be observed in the 1600°C sample. These α-Al_2O_3-free zones are formed only when fibres and matrix are in direct contact (Fig. 4). For comparison, Nextel 720 fibres alone were fired at 1600°C (Fig. 5). No depletion of α-Al_2O_3 occurs in the fibre rim area.

Fig. 6 provides information on the temperature-dependent development of the chemical composition of the matrix in its entirety and of the matrix mullite crystals, respectively. The bulk composition was determined by EDX analyses of relatively large (5 μm diameter or more) matrix agglomerates, each of them containing numerous mullite crystals and glassy areas. The mullite

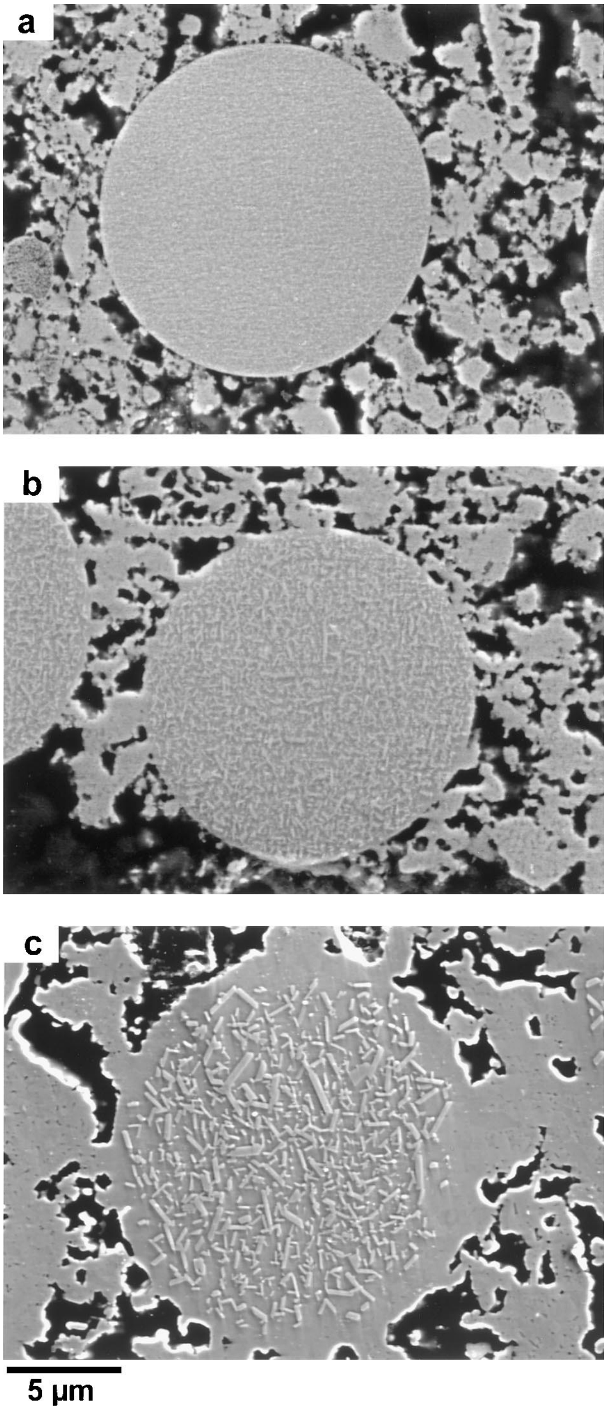

Fig. 3. Microstructural changes of alumino silicate fibre/porous mullite matrix composite caused by thermal treatment. (a) as-prepared; (b) 1500°C, 2 h; (c) 1600°C, 2 h. Note that with increasing temperature, gradual coarsening of the fibre compounds occurs. At 1600°C, a depletion of α-Al_2O_3 in the fibre rim area is observed.

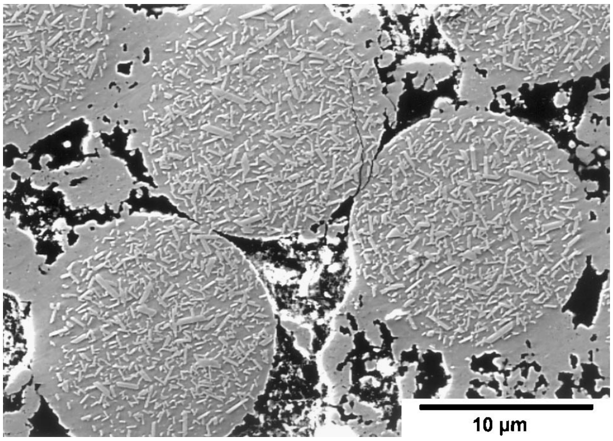

Fig. 4. Alumino silicate fibre/porous mullite matrix composite heat-treated at 1600°C (2 h). Note that the α-Al_2O_3 free fibre rims are formed only in areas of fibre/matrix contact.

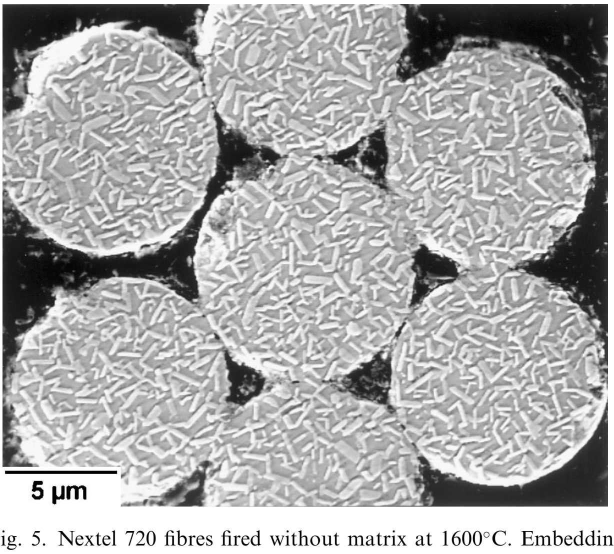

Fig. 5. Nextel 720 fibres fired without matrix at 1600°C. Embedding the fibres in epoxy allows the preparation of a polished cross-section. No α-Al_2O_3 free fibre rims occur in contrast to Fig. 3.

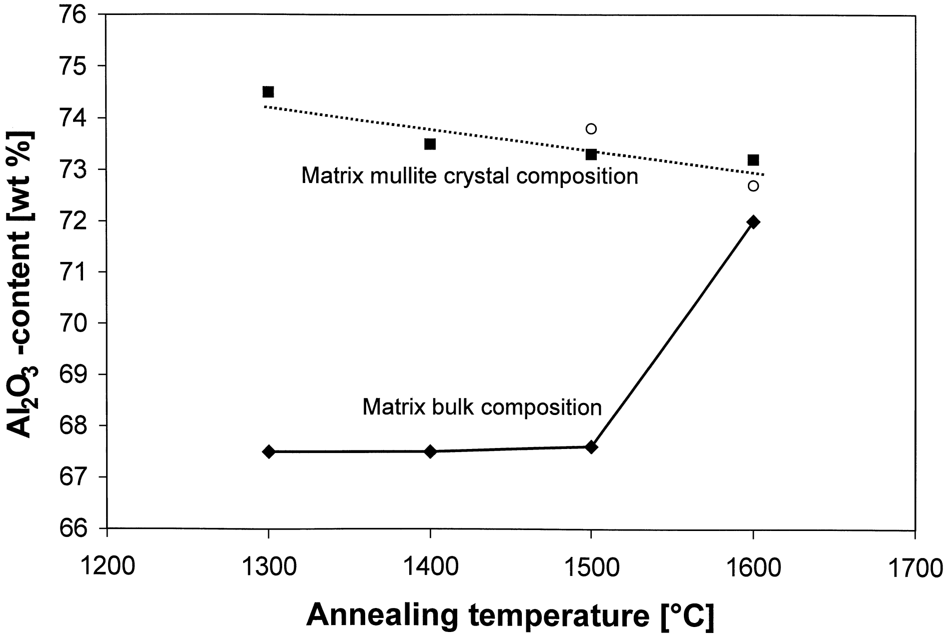

Fig. 6. Matrix bulk composition (i.e. mullite plus vitreous phase) and matrix mullite composition of alumino silicate fibre/porous mullite matrix composite plotted as a function of temperature. Rhombs: matrix composition as determined by SEM-EDX. Squares: mullite composition on basis of lattice constant data. Open circles: mullite composition analyzed by TEM-EDX.

crystal composition was determined via mullite lattice constants by X-ray methods using fibre-free reference matrix material and was checked in composite samples by EDX analyses in combination with transmission electron microscopy. The matrix mullite crystals of the as-prepared material are relatively alumina-rich (74.5 wt.% Al_2O_3) with respect to stoichiometric mullite (72 wt.% Al_2O_3). Treatment at higher temperatures leads to a gradual development towards the Al_2O_3/SiO_2 ratio of stoichiometric mullite. On the other hand, the matrix bulk composition of samples fired below 1500°C, is relatively poor in Al_2O_3 (ca. 68 wt.% Al_2O_3). Firing at 1600°C, however, causes a drastic change of the matrix composition: mullite crystals and matrix display virtually the same composition with about 72 wt.% Al_2O_3.

Fig. 7 shows the fibre/matrix interface area of a sample heat-treated at 1300°C for 1000 h. A reaction zone, free in α-Al_2O_3, becomes visible in this material though the zone's extension is smaller than oberved in the sample heat-treated at 1600°C, 2 h. Load/deflection curves of the porous mullite composites heat-treated at various temperatures are plotted in Fig. 8. Bending tests signal non-brittle (damage-tolerant) fracture behavior of the composites up to 1500°C though the maximum strength values slightly decrease with increasing temperature. Firing at 1600°C, on the other hand, leads to brittle

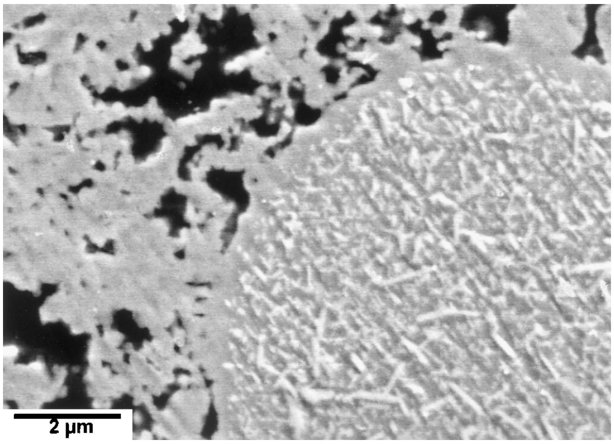

Fig. 7. Fibre/matrix interface area of alumino silicate fibre/porous mullite matrix composite heat-treated at 1300°C for 1000 h. Note the formation of an α-Al_2O_3 free fibre rim.

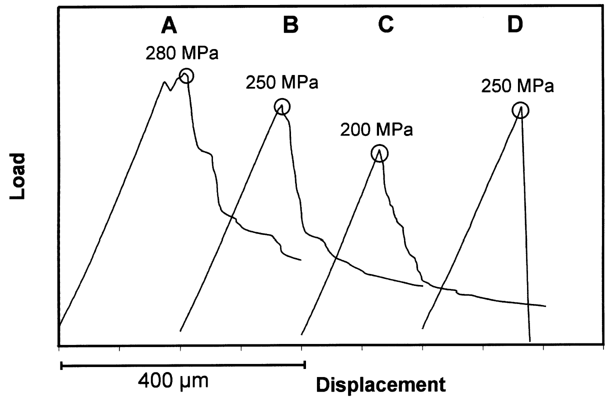

Fig. 8. Load/deflection curves of alumino silicate fibre/porous mullite matrix composites fired at various temperatures (2 h) (A) as-prepared; (B) 1400°C; (C) 1500°C; (D) 1600°C.

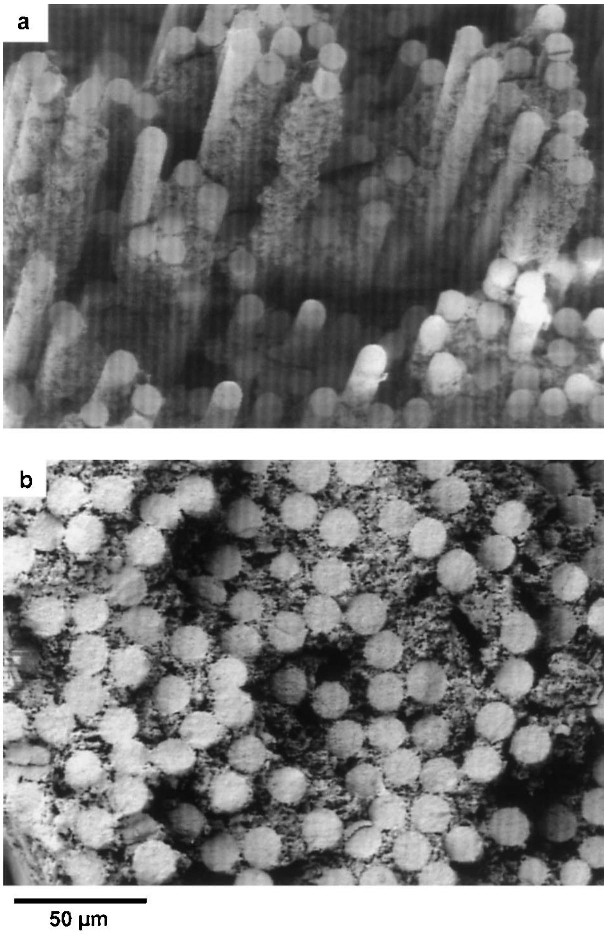

Fig. 9. Fracture surfaces of alumino silicate fibre/porous mullite matrix composites. (a) As-prepared; (b) 1600°C (2 h).

failure of the composites though the strength value slightly increases. Fracture surfaces of the as-prepared composite and of a specimen heat-treated at 1600°C are shown in Fig. 9. While the as-prepared ceramic matrix composite exhibits a fracture surface with delamination effects and fibre pull-out that signals energy-dissipating fracture mechanisms, the 1600°C sample produces a smooth fracture surface similar to those of brittle monolithic ceramic materials.

4. Discussion

Microstructural and microchemical analyses of the aluminum silicate fibre/porous mullite composite reveal reactions between matrix and fibres above about 1500°C. Obviously, the free silica phase[‡] of the matrix is transported towards the fibre surface and mullite is formed in a peripheral area of the fibres according to the reaction 2 $SiO_2 + 3\ \alpha\text{-}Al_2O_3 \Rightarrow 3Al_2O_3 2SiO_2$. At the end of this process, the SiO_2 phase of the matrix is fully consumed. The reaction is virtually complete above about 1600°C, since bulk matrix and matrix mullite compositions then are nearly the same (Fig. 6) indicating that no "free" SiO_2 phase is present any more. Starting from a fibre content of 70 wt.%, the following phase ratio of the composite can be estimated on basis of fibre and matrix compositions for $T = 1500°C$, i.e. just below the fibre/matrix reaction process:[§] about 67 wt.% mullite (occurring in the matrix and in the fibres), about 2 wt.% of free silica (occurring in the matrix), about 31 wt.% α-Al_2O_3 (occurring in the fibre).

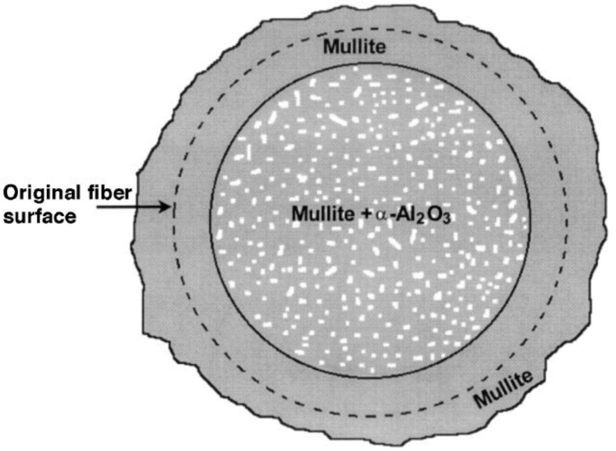

Fig. 10. Schematic presentation of the mechanism of fibre/matrix interaction in alumino silicate fibre/porous mullite matrix composite. Note that the fibre diameter gradually increases with the degreee of reaction (see also Fig. 3).

If all free silica has been reacted to mullite the total α-Al_2O_3 fraction of the composite is reduced from ≈31 to ≈26 wt.% since one mass unit of SiO_2 consumes 2.57 mass units of α-Al_2O_3. Thus, one sixth of the original fibre cross-section should be affected by the α-Al_2O_3 consumption corresponding to a 0.5 µm zone on the periphery of the 10 µm thick fibre. However, due to the addition of SiO_2 from the matrix and subsequent mullitization, the fibre diameter increases (each volume unit of α-Al_2O_3 reacting with silica forms 1.8 volume units of mullite) and the newly formed mullite zone becomes about 1 µm thick (see Fig. 10). The present results demonstrate that this is actually the case (Figs. 3c and 4).

Reactions between free silica and α-Al_2O_3 were investigated by several authors.[12–15] Johnson and Pask described newly formed mullite directly at the α-Al_2O_3/SiO_2 interface. Closer inspection by means of analytical

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[‡] For simplification, the glassy phase of the matrix is called "silica phase" or "free silica" even though a small percentage of alumina is incorporated in this glass.

[§] A mullite composition of 73 wt.% Al_2O_3, 27 wt.% SiO_2 was assumed for mullite occurring in the fibres and in the matrix. Mullite crystals in as-received Nextel 720 fibres are much richer in Al_2O_3 but develop towards stoichiometric composition when heated at 1500°C.[17] A similar tendency, although less pronounced, can be observed in the sol–gel derived mullite matrix (see Fig. 6).

TEM, however, showed that the mullite nucleation occurred inside the glassy phase rather than in direct contact with the α-Al_2O_3 grains. Microstructural evidence suggested that Al_2O_3 was solved in the coexisting non-crystalline silica phase and mullite nucleation occurs as soon as Al_2O_3 supersaturation is reached.[15] In the present study, mullite formation inside the glassy pockets of the fibres has never been observed. Since mullite grains a priori are in contact with both, SiO_2 (matrix) and α-Al_2O_3 (fibres), it is concluded that no mullite nucleation took place. We believe, instead, that growth of the pre-existing mullite grains by interdiffusion of Si^{4+} and Al^{3+} occurred. The driving force for interdiffusion of Si^{4+} and Al^{3+} in mullite crystals is obviously the occurring concentration gradient ranging from ≈72 wt.% Al_2O_3 (mullite in contact with SiO_2) to ≈74 wt.% Al_2O_3 (mullite in contact with α-Al_2O_3; see Fig. 11). According to this model, mullitization starts at the interfacial area of fibres and matrix. The matrix thereby acts as a silica reservoir when the SiO_2 located directly at the fibre/matrix boundary is consumed. During the reaction process, the viscous silica-rich phase is presumably transported towards the fibre surface by capillary forces. Reaction kinetics can be estimated assuming $Q = 700$ kJ/mol as a typical value of activation energy for diffusional processes in mullite.[16] Using this activation energy value, a temperature increment of 25°C corresponds to a doubling of the reaction rate, and 1000 h annealing at 1300 °C corresponds to 2 h firing at 1525° C, respectively. The microstructural observation is in good accordance to this estimation (Figs. 7 and 3c): samples annealed for 1000 h at 1300°C do display reaction zones at the fibre rims but the zones are smaller than these of samples thermally treated for 2 h at 1600°C.

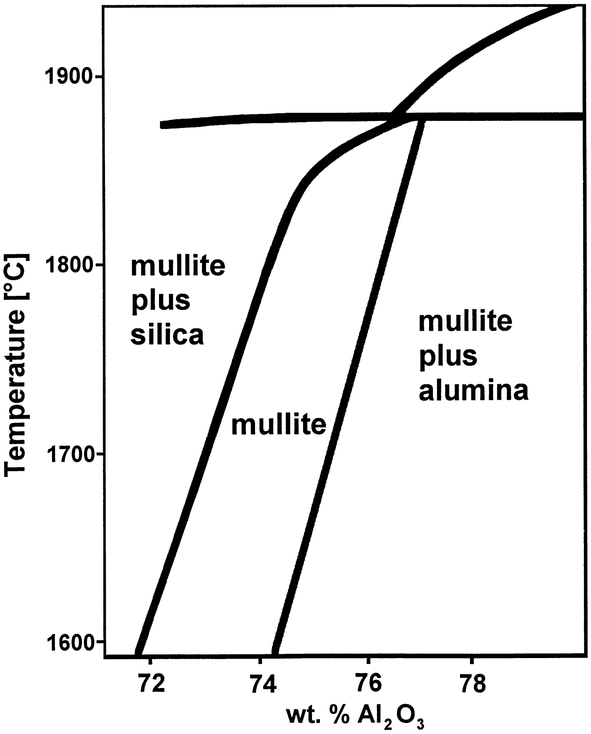

Fig. 11. Mullite stability region of the SiO_2–Al_2O_3 phase diagram (after Klug et al.[18]).

Load/deflection curves of the porous mullite matrix composites heat-treated at various temperatures signalize a damage tolerant fracture behaviour up to 1500°C (Fig. 8). A 25% decrease in maximum strength occurs after firing at 1500°C with respect to the starting material. Interestingly enough, Nextel 720 fibres alone undergo a 60% strength degradation after a 1500°C heat-treatment.[17] Obviously, the strength of the composites fired up to 1500°C is not controlled by direct fibre strength but fibre/matrix delamination will occur as the first step of failure. The damage tolerant fracture behaviour of the composite after reaching maximum load is controlled by crack bridging, multiple cracking and fibre pull-out, which is demonstrated by a typical fracture surface (Fig. 9a). Firing at 1600°C, on the other hand, leads to the above described reactions in the fibre/matrix interfacial area and hence bonding between matrix and fibres drastically increases. As a consequence, the material becomes brittle as can be clearly derived from the load/deflection curves (Fig. 8) and by the resulting flat fracture surface (Fig. 9b).

It is an important result of this study that only little thermally-induced degradation of the porous matrix composite occurs unless interactions between fibres and matrix take place. This favorable behavior is explained by the fact that thermal activation of reactions between vitreous SiO_2 and α-Al_2O_3 is considerably high. According to the present study, the thermal stability of the Nextel 720 fibre reinforced porous mullite matrix composites is estimated to be 1500°C in the case of short-term application (several hours) or 1300°C for long-term applications (1000 h and more).

Acknowledgements

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