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Aluminosilicate fiber/mullite matrix composites with favorable high-temperature properties

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Abstract

Oxide-based ceramic matrix composites with a highly porous mullite matrix and Nextel™ 720 alumino silicate fibers have been fabricated by infiltrating filaments with a mullite precursor slurry, and by subsequent one-dimensional (1D) and two-dimensional (2D)-winding up the fiber bundles on mandrels. The green bodies were pressureless sintered in air at 1300°C. These composites which require no fiber/matrix interface are characterized by favorable damage tolerance and bending strengths of 160 MPa at room temperature and up to temperatures of 1200°C. These properties make it an excellent low-cost choice for combustion chamber liners, diffusor rings and other thermal protection systems for high temperature applications in oxidizing environment.

Keywords: Aluminosilicate fibres; Composites; Mechanical properties; Mullite matrix; Sintering

1. Introduction

Oxide-based continuous fiber reinforced composites are ideally suited for use in applications demanding long-term high-temperature (< 1300°C) stability in oxidizing atmosphere, damage tolerance and high thermal shock resistance suitable for applications such as in thermal protection systems for combustion chambers in aircraft engines. It has been demonstrated recently that mullite fiber/mullite matrix composites with acceptable strength and damage tolerance can be fabricated through hot-pressing, provided that fibers are coated with, e.g. monazite,[1] boron nitride,[2] β-alumina or fugitive layers using chemical dip coating or CVD processes. However, the disadvantages of these composites are the complex high-cost fiber-coating and hot-pressing technique, which often cannot be used where near-net shaping is required.

Recently, new concepts for damage-tolerant ceramic-matrix composites (CMCs) without fiber-coating have been developed. Lange et al.[3] described an oxide/oxide system with a porous matrix, which exhibited high strength and non-brittle failure. The matrix comprises a stable porous framework and an infiltrated, pyrolyzed precursor. Levi et al.[4] introduced an all-oxide composite similar to SiC/carbon or carbon/carbon systems where a relatively inhomogeneous microstructure containing fiber-rich and fiber-poor regions promote crack deflection and results in a high work of fracture. The concept of porous matrix composites via matrix infiltration and pressureless sintering has been further developed by Harrison et al.[5] and Tu et al.[6]

2. Experimental procedure

2.1. Sample preparation

Alumino silicate fibers (Nextel 720, 3M Corp. Minneapolis, USA) were selected because of their high-temperature stability and creep resistance. Data published by the manufacturer, show that Nextel 720 fibers are composed of 85 wt% Al_2O_3 and 15 wt% SiO_2 in the form of mullite and corundum.[7] Commercial 400-denier yarn was used, with the sizing previously removed by thermal exposure in an initial processing step. The slurry was based on a commercial Type-2 mullite precursor (Siral 28 l/32 Condea Chemistry Corp., Hamburg,

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Germany[8]). The steps involved in slurry preparation are outlined in Fig. 1.[9] Siral powders (400 m^2/g) were first calcined in order to decrease the surface area and to minimize the slurry viscosity. Optimized calcination conditions in terms of both high residual sintering activity and small particle size were realized at 1150°C (5 h). In order to destroy agglomerates, calcined powders were dry-milled in a planetary ball mill with 5-mm diameter Si_3N_4 milling balls in a teflon vessel. Equal amounts of milling media and powder were used. De-agglomerated powders were blended with a water-based solution containing binder, surfactant, emulsifier and 8 to 16 wt% of liquefying agent. This mixture was also homogenized for 1 h in a planetary ball mill. For impregnation of fiber tows, the slurry solid content was set to 45 wt% with a viscosity of 0.07 Pas and a pH of 6.6.

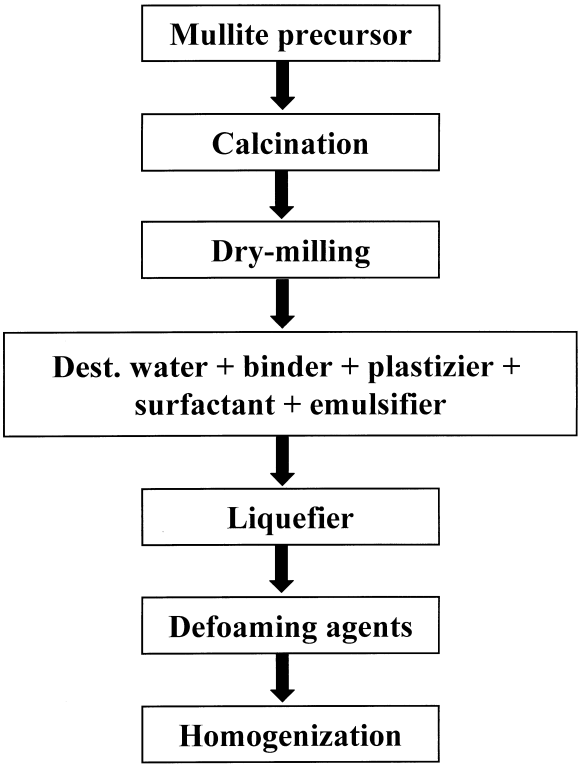


Fig. 1. Schematic flow sheet of slurry preparation.

Composite components were fabricated by infiltration fiber bundles with the precursor slurry and a subsequent winding-up process, as outlined in Fig 2. Filament winding was conducted with a winding equipment developed in-house at the Institute for Materials Research at DLR. Sizing of the as-received Nextel 720 fibers was burned-off in a tube furnace at 1100°C. Fiber bundles were then mechanically spread apart and infiltrated with a water-based matrix slurry. In the next step, the roving was passed through a microwave furnace (AGNI, Thermal and Materials Technology, Aachen) to partially dry the bundles in order to yield a relatively high matrix content between individual fibers. Finally, fibers were wound on a plastic mandrel (diameter = 20 to 200 mm) with a constant fiber tension of about 30 MPa (see Fig. 2). The rotation speed and traverse speed of the mandrel were adjusted for controlled fabrication of composites with 1D- and 2D-fiber orientations. Tubes with different diameters and lengths were produced by drying the green bodies on the mandrel. Green bodies could also be removed from the mandrel in the wet state, creating stackable unidirectional prepreg tapes or other more complex shapes. Once in their final shape, the green bodies were pressureless-sintered in air, e.g. at 1300°C for 15 min with a heating rate of 10°C/min, producing as-sintered composites with a fiber content < 50 vol % (Fig. 3).

2.2. Characterization

Mechanical properties of samples were determined from bars of 1D reinforced composites (50×5×1.8 mm). Fracture strength was measured in three-point bending tests with a span of 40 mm.

Room-temperature tests were conducted on as-sintered specimens, and after 1250°C/400 h and 1500°C/3 h exposure, respectively. High-temperature bending tests were carried out on specimens heated in a SiC induction furnace with a heating rate of 50°C/min and a crosshead speed of 0.5 mm/min. All test samples were produced from the same batch to allow for direct comparison of results.

The microstructure of sintered samples was studied by optical microscopy and field emission scanning electron

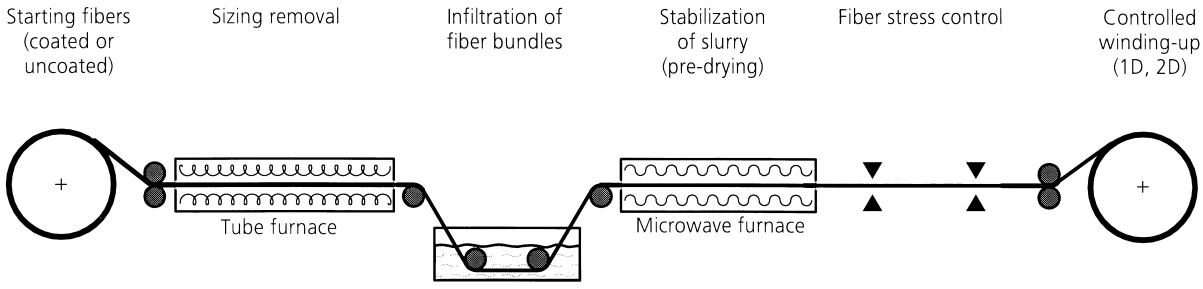
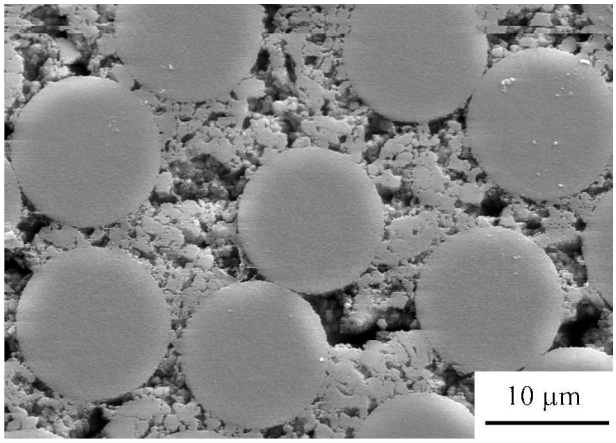
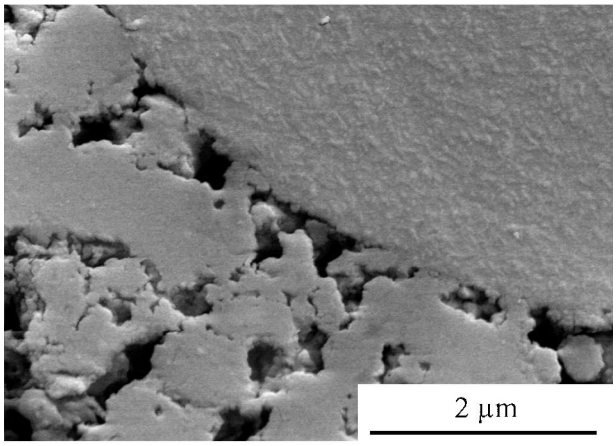


Fig. 2. Schematic view of the fabrication route of the aluminosilicate fiber/mullite matrix composites.



(a)



(b)

Fig. 3. Scanning electron micrographs from polished sections of the as-sintered (1300°C, 1 h) 1D aluminosilicate fiber (Nextel 720)/mullite matrix composite in a view perpendicular to the fiber axes. The fibre content is 50 vol%; the highly porous matrix corresponds to a theoretical density of 50%; (a) overview; (b) fiber/matrix contact points.

microscopy (Leitz LEO 982, Germany) or polished sections, while phase composition were determined using X-ray diffractometry (XRD) (Siemens D 5000, Germany).

3. Results and discussion

Fig. 4 shows the typical stress–deflection curve of the Nextel 720 fiber/porous mullite matrix composite determined by three-point bending. Up to the maximum stress of about 160 MPa, the material displayed linear-elastic deformation behavior. At the point of maximal stress, the first matrix cracks occur, indicated by a stepwise decrease of stress during further deflection of the bending bar. This type of stress–deflection curve corresponds to a pseudoplastic, damage tolerant behavior of the composite. In-situ high-temperature tests at 1200°C showed that there is no distinct change of this behavior with respect to room-temperature experiments. The good high-temperature properties of the composite have been proved by long-term heat treatments (1250°C/400 h), and by short-time experiments at very high temperature (1500°C/3 h). These materials still exhibits maximum stresses of about 150 MPa, and a pseudoplastic, damage-tolerant behavior (see Fig. 5). The favorable mechanical behaviour of the composites is attributed to the specific fiber/matrix ratio. Using the rule of mixture of fibers (50 vol%) and matrix (50 vol%), and taking into account a constant fiber and matrix strain in the composite, fiber and matrix stresses should correlate with the respective Young's moduli. Due to the high value of the fiber modulus ($E_f = 260$ GPa) and the relatively low one of the porous mullite matrix ($E_m = 46$ GPa), the fibers must transfear the major part of the applied stress.

Starting from a fiber strength of 2000 MPa,[10] fiber damage should occur at a matrix stress level of about 354 MPa, which is definitely higher than the strength of the porous mullite matrix. This means that the damage behavior of the composites is mainly controlled by the matrix and, on the other hand, fiber damage has a negligible influence only. This may be the reason why the short-time high-temperature treatment of the composite at 1500°C does not decrease its mechanical properties drastically.

We believe that the favorable mechanical behavior of the composites is due to their microstructure. Pressureless-sintered composites (1300°C/1 h) are characterized by high fiber contents (< 50 vol%) and by matrices consisting of mullite, with fine and homogeneously distributed pores (matrix porosity > 50 vol%). The matrix framework with low fracture energy enables easily working crack deflection and dissociation within the matrix, especially along the fibers. Therefore, no special, mechanically-weak fiber coatings are required. On the other hand, the local contact points between fibers and matrix are obviously firm enough to effectively transfer load between matrix and fibers. Both points are responsible for the favorable strength and the damage tolerance of the composites, and their astonishingly high temperature stability.

Levi et al.[4] produced similar porous matrix composites but with Nextel 610 (α-Al_2O_3) fibers instead of the Nextel 720 aluminosilicate fibers. These composites showed higher mechanical strengths at room temperature than our aluminosilicate fiber/mullite matrix composites. This probably relates to the higher Young's modulus of α-Al_2O_3 fibers. Because of the mismatch in thermal expansion of α-Al_2O_3 and mullite, there is a thermally-induced compressive matrix stress upon post-processing cool down of the composites. This mismatch provides high strength at low temperature. Above processing temperatures, however, the thermal expansion mismatch reduces strength as compressive stresses

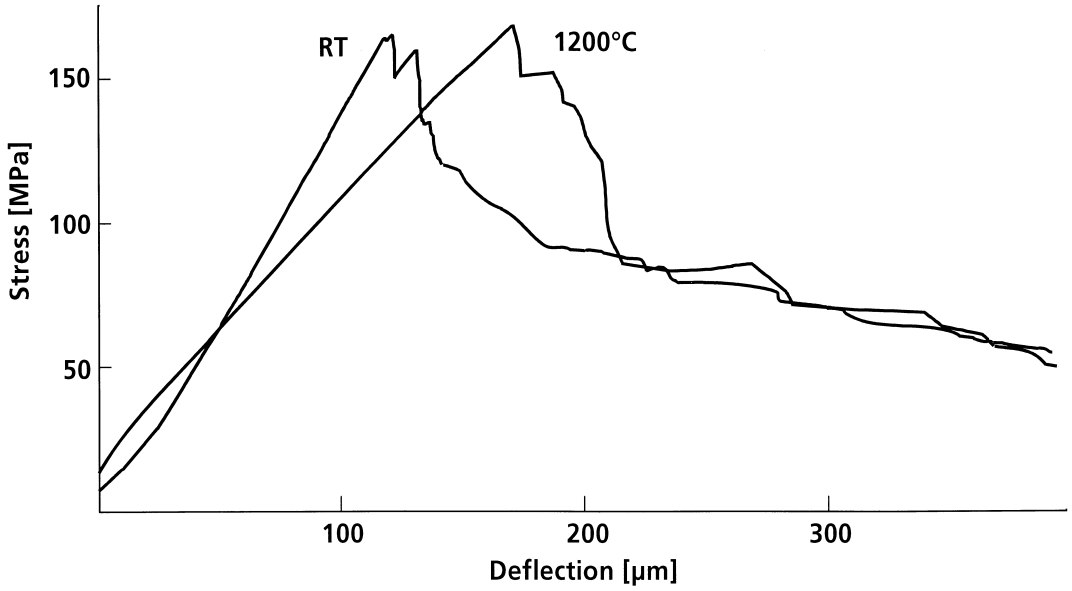


Fig. 4. Stress–deflection curves of the 1D aluminosilicate fiber/mullite matrix composites at room temperature and at 1200°C obtained from three-point bending tests.

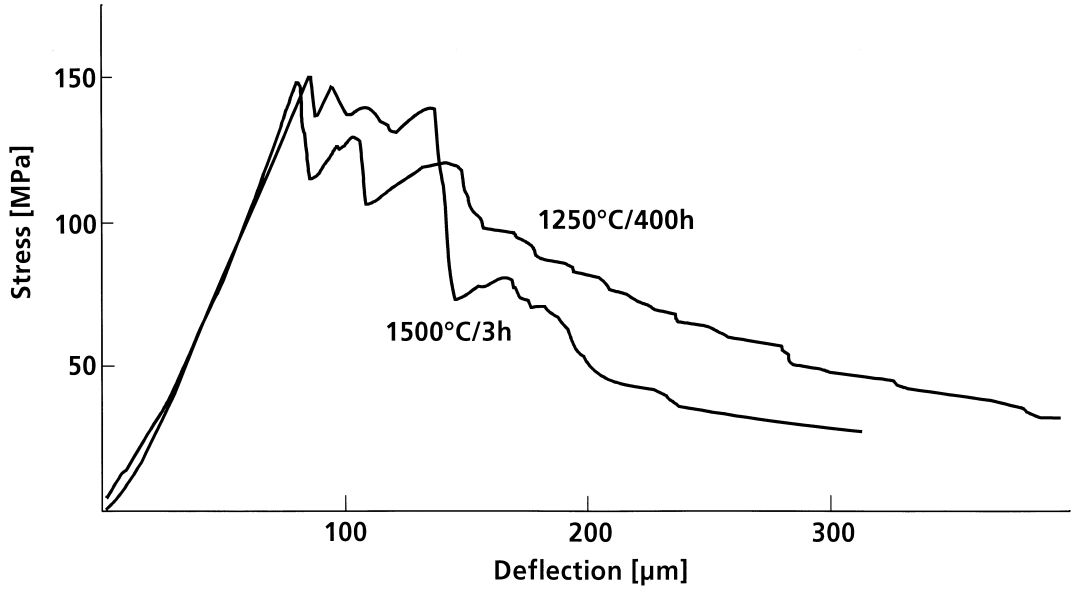


Fig. 5. Stress–deflection diagrams of heat-treated (1250°C/400 h; 1500°C/3 h) 1D aluminosilicate fiber/mullite matrix composites obtained by three-point-bending at room temperature.

change into tensile stresses producing unfavorable thermo-mechanical properties. Furthermore, the low high temperature creep stability of α-Al_2O_3 fibers make alumino-silicate fibers a better choice for many applications, in particular for long-term use in gas turbines.

4. Conclusions

A novel aluminosilicate fiber/mullite matrix composite was produced, based on a high content of Nextel 720 fibers and a highly porous mullite matrix. The composite exhibited a damage-tolerant behavior and retains RT maximum bending strength (160 MPa) up to 1200°C. Long-term heat treatment at 1250°C and short-term heat treatment at 1500°C had no effect upon RT behavior. Due to weak fiber/matrix bonding, the use of a fiber-coating was not necessary. Since fairly simple fabrication techniques were used (e.g. filament winding and pressureless sintering), processing was easily adaptable to the fabrication of many different shapes, including tubes, rings and plates.

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