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High Temperature Behaviour of Polycrystalline Aluminosilicate Fibres with Mullite Bulk Composition. I. Microstructure and Strength Properties

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Abstract

Temperature-dependent microstructure/strength relations of commercial aluminosilicate fibres with near-stoichometric mullite bulk composition are investigated.

As-received Nextel 440™ fibres (70 wt% Al_2O_3, 28 wt% SiO_2, 2 wt% B_2O_3), consisting of nanometre-sized γ-Al_2O_3 and a minor amount of amorphous phase, have tensile strength of 2100 MPa. Heat treatment at 1200°C causes transformation into fine-grained mullite (mean grain size: 80 nm). The remaining tensile strength is 1600 MPa. Heat treatment at higher temperatures leads to considerable reduction of strength (1100 MPa after firing at 1400°C) attributed to mullite grain coarsening (mean grain size at 1400°C: 135 nm).

Altex 2K fibres (72 wt% Al_2O_3, 28 wt% SiO_2) consist of single-phase mullite with a mean grain size of 115 nm. Tensile strength is comparatively low (1250 MPa). Annealing at 1000°C causes a significant increase in strength (1600 MPa). Above 1200°C mullite coarsening and strength reduction are similar to those of Nextel 440 fibres.

1 Introduction

Aluminosilicate fibres are used in a wide variety of high temperature applications, e.g. for thermocouple insulations, furnace seals and filter bags.[1] Another promising application of aluminosilicate fibres is the reinforcement of ceramic matrices in composites (see, for example, Ref. 2). Aluminosilicate fibres of mullite bulk composition may consist of non-crystalline precursor states, of nanocrystalline γ-Al_2O_3 plus SiO_2 phase assemblages or of microcrystalline mullite. Due to their phase compositions and/or small crystal sizes, the microstructures of these fibres are not stable thermodynamically: by heat treatment at sufficiently high temperature, phase transformations and grain coarsening occur which in most cases are harmful for the mechanical properties of the fibres. Detailed knowledge of the temperature-dependent microstructures and strengths is therefore essential for the prediction of possible applications of the fibres in high temperature composites.

2 Experimental

2.1 Sample material

Two types of technical aluminosilicate fibres were investigated: Nextel 440™ (3M, St. Paul, MN, USA) with 70 wt% Al_2O_3, 28 wt% SiO_2, 2 wt% B_2O_3[1] and Altex 2K (Sumitomo Chemical Inc., Osaka, Japan) with 72 wt% Al_2O_3 and 28 wt% SiO_2. Nextel 440 fibres have elliptical cross-sections with 7 and 12 μm diameters and consist of transition alumina (designated as γ-Al_2O_3 in the following) and silica-rich glassy phase. Sumitomo Altex 2K fibres have circular cross-sections with a mean diameter of 12 μm, and consist of single-phase mullite. Both fibre materials were annealed in air in an induction heated laboratory furnace at 1000, 1100, 1150, 1200, 1300, 1400, 1500, 1600°C for 4 h in each case.

2.2 Single fibre tensile strength measurements

Room temperature strengths of the fibres annealed for 4 h at various temperatures were determined, based on at least 30 individual measurements in each case. Single fibres were glued on a paper bridging the centre of a circular hole (diameter $\approx$ 5 mm). On both sides of the hole the paper was separated and bridged by a polymer fibre. The arrangement was installed in a tensile testing equipment with a load cell for very small loads. After fixing the holder the polymer fibres were melted and special care was taken that the test fibre was not damaged by this procedure. Tensile tests were performed under a constant crosshead speed of 0·2 mm min^{-1}. Actual tensile strength

values of fibres were then calculated considering individual fibre cross-sections measured by scanning electron microscopy. Elliptical cross-section areas of Nextel fibres were determined according to the procedure described by Fernando *et al.*[3]

2.3 Microstructural characterization of fibres

Due to the small grains occurring in all fibres, microstructures were examined by transmission electron microscopy (TEM, Philips EM 430) with an accelerating voltage of 300 kV. Electron transparent areas in long sections of the fibres were achieved by Ar-ion beam milling. Based on TEM photographs, grain area distributions of starting materials and of heat-treated fibres were calculated by means of a Synoptics-Semper 6 image processing system using at least 100 grain area values. Diameter distributions and mean grain sizes for each sample were calculated neglecting intersectional effects.

Information on the temperature-dependent phase compositions were obtained by X-ray powder diffractometry. Studies were carried out with a computer-controlled Siemens D 5000 powder diffractometer using Ni-filtered CuK_α radiation. Diffraction patterns were recorded in the 2θ range from 10 to 80°, in step scan mode.

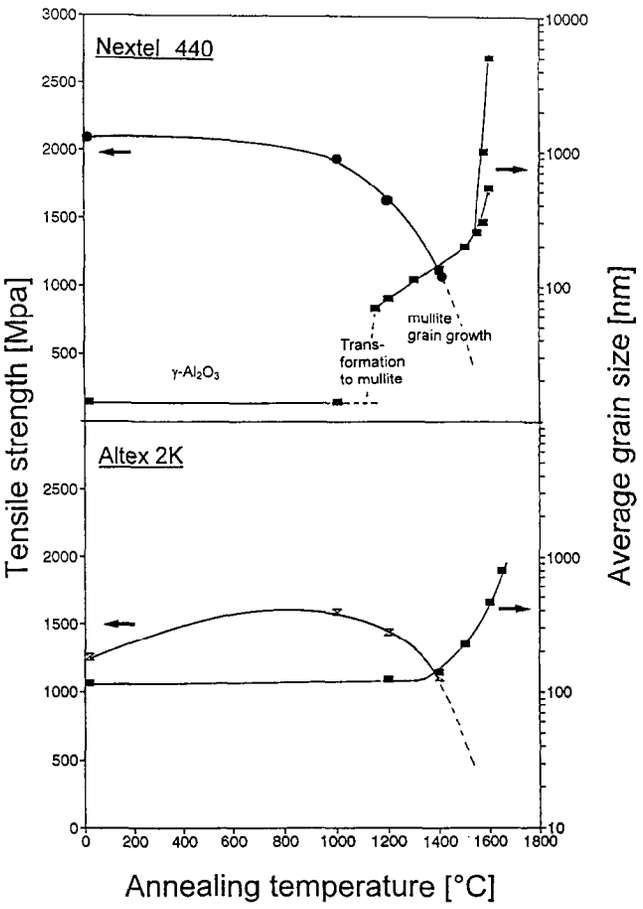


Fig. 1. Grain size and strength of Nextel 440 and Altex 2K fibres heat-treated between 1000 and 1600°C.

3 Results

3.1 Tensile strengths of fibres

Tensile strengths of Nextel and Altex fibres as-received and heat-treated at 1000, 1200 and 1400°C are given in Table 1 and Fig.1. The tensile strength of Nextel fibres in the as-received state is >2 GPa. This value remains nearly constant up to 1000°C heat treatment. At higher annealing temperatures, however, the tensile strength decreases. Tensile strength of as-received Altex 2K fibres is significantly lower than that of Nextel 440 fibres. The strength of the Altex fibres annealed at 1000°C significantly increases with respect to the starting material, whereas the value of the 1200°C sample is similar to that of the as-received material. Distinct strength reduction is observed in Altex 2K fibres heat-treated at 1400°C. Above 1400°C, both fibres become so brittle that handling with regard to the testing facilities was not possible, which indicates drastic decrease in strength.

3.2 Phase content and microstructural development of fibres

3.2.1 Nextel 440 fibres

According to phase content and microstructure, the temperature-dependent development of the Nextel 440 fibres can be subdivided into three stages (Fig. 1): 'γ-Al_2O_3 + SiO_2 stage'; 'γ-Al_2O_3 + SiO_2 to mullite transformation stage'; and 'mullite grain growth stage'.

(a) γ-Al_2O_3 + SiO_2 stage. The γ-Al_2O_3 + SiO_2 region extends from the as-received state up to ≈1100°C. A typical microstructure of this stage is given in Fig. 2, showing equiaxed γ-Al_2O_3 crystallites with an average grain size of 15 nm. Annealing up to 1100°C causes no coarsening of the γ-Al_2O_3 nanocrystals.

Table 1. Tensile strength of Nextel and Altex 2K fibres as-received and heat-treated at different temperatures

	as-received		*1000°C*		*1200°C*		*1400°C*	
	Nextel	*Altex*	*Nextel*	*Altex*	*Nextel*	*Altex*	*Nextel*	*Altex*
σ_m (MPa)	2086	1253	1954	1594	1635	1439	1117	1108
Weibull parameter, m	4·9	6·1	6·0	5·8	4·6	5·1	6·1	5·7

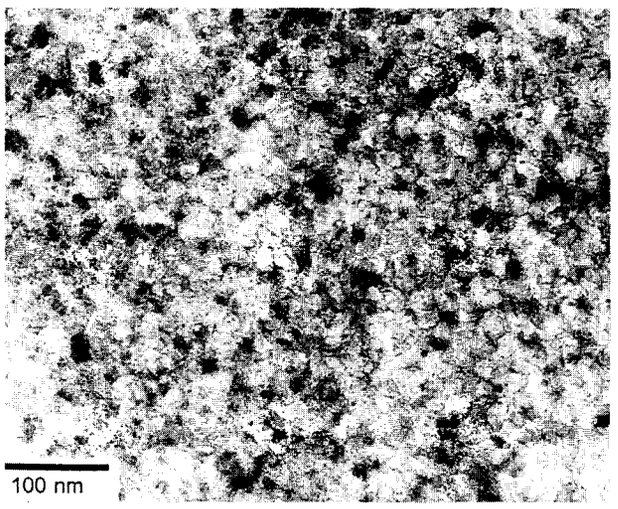


Fig. 2. Micrograph (TEM) of as-received Nextel 440 fibres: nanosized γ-Al_2O_3 crystals.

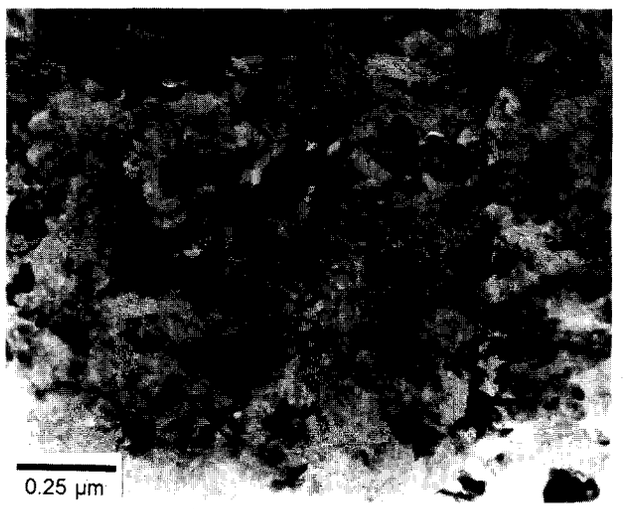


Fig. 4. Micrograph (TEM) of Nextel 440 fibres heat-treated at 1200°C, 4 h: irregular-shaped mullite grains.

(b) γ-Al_2O_3 + SiO_2 to mullite transformation stage. The γ-Al_2O_3 + SiO_2 to mullite transformation region extends from ≈1100 to 1200°C. In samples heat-treated at 1100°C small mullite crystals are occasionally detected by means of convergent beam diffraction or lattice fringe imaging (Fig. 3). With increasing temperature the mullite content gradually increases. A detailed analysis of the γ-Al_2O_3 + SiO_2 to mullite transformation behaviour is presented in the second part of this study.[4]

(c) Mullite grain growth stage. This region refers to annealing temperatures > 1200°C, where distinct mullite grain coarsening occurs. Microstructures of Nextel 440 fibres completely transformed to mullite by heat treatments at 1200, 1400 and 1600°C are shown in Figs 4 to 6. Firing at 1200°C leads to irregular-shaped mullite crystals with an average grain size of 80 nm (Fig. 4). After firing at 1400°C the mean grain size of mullite has increased to 135 nm and the crystals develop more regular polygonic shapes [Fig. 5(a)]. At triple grain junctions glassy phase is detected [Fig. 5(b)]. Above 1550°C exaggerated grown mullite crystals

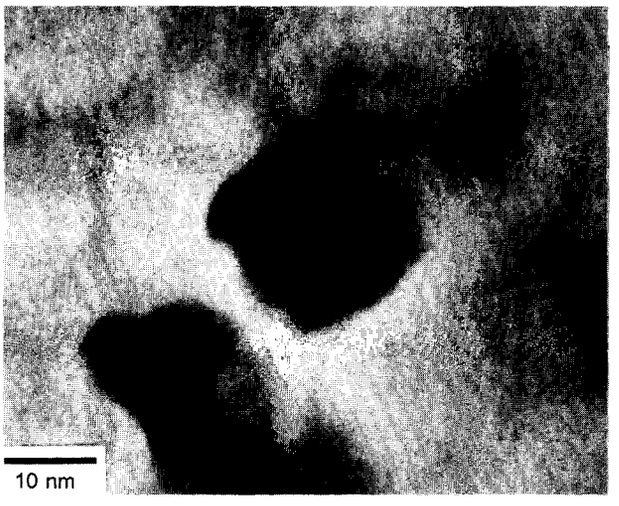
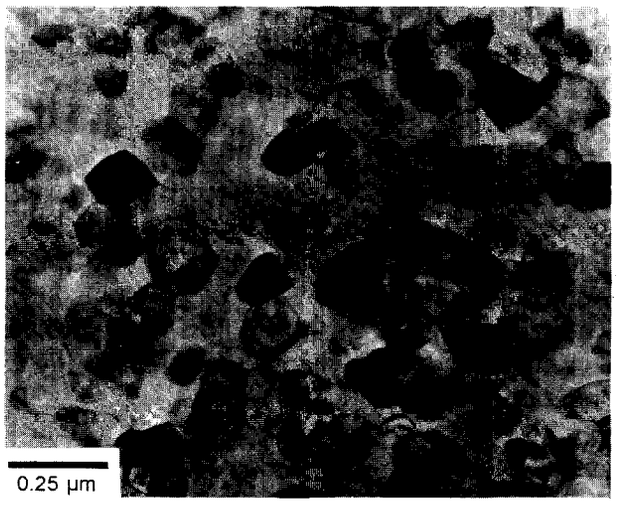
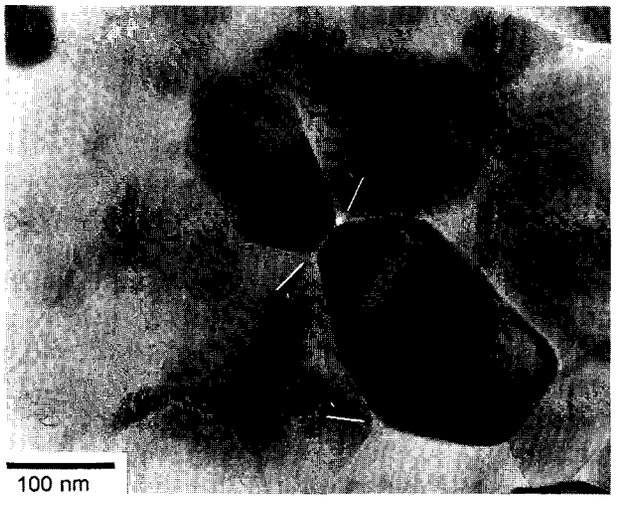


Fig. 3. Micrograph (TEM) of Nextel 440 fibres heat-treated at 1100°C, 4 h: small mullite crystal with (1 0 0) lattice fringes.



(a)



(b)

Fig. 5. Micrographs (TEM) of Nextel 440 fibres heat-treated at 1400°C, 4 h: (a) coarsened polygonic mullite grains; (b) glassphase at triple grain junctions (arrows).

Fig. 6. Micrograph (TEM) of Nextel 440 fibres heat-treated at 1600°C, 4 h: secondary grain growth of mullite.

are observed which are embedded in a finer grained matrix (Fig. 6). The bimodal grain size distribution leads to the split grain size curve at ≥1550°C (Fig. 1): the upper branch corresponds to the large secondary mullite grains, while the lower one represents the unconsumed primaries.

3.2.2 Altex 2K fibres

The microstructure of the as-received Altex 2K fibres is similar to that of Nextel 440 heat-treated at 1200°C, i.e. containing irregular-shaped mullite grains with a mean grain size of ≈115 nm. Heat treatments at 1000°C and 1200°C cause no distinct microstructural change, but above 1200°C moderate grain coarsening occurs (Fig. 1). The average grain sizes and strengths of Altex fibres fired at 1400°C are very similar to those of Nextel 440 fibre heat-treated under the same conditions. However, secondary growth of mullite grains does not occur in Altex 2K fibres even at 1650°C.

4 Discussion

Only γ-Al_2O_3 could be detected by TEM in the as-received Nextel 440 fibres, although, according to the bulk composition, SiO_2 is present at 28 wt%. Though a certain amount of SiO_2 is known to be incorporated in the alumina phase,[5] a remaining fraction must occur, presumably as very thin (~ 1 nm) non-crystalline layers which are not detectable by our TEM analyses of the nanocrystalline material.

These amorphous films surrounding the transition alumina grains may explain the stability of the nanocrystalline microstructure up to 1100°C: obviously the high Si–O bond strength[6] within the SiO_2 films may cause them to act as diffusion barriers, thus preventing crystal coarsening. On the other hand, the occurrence of amorphous films enveloping γ-Al_2O_3 crystallites considerably reduces the mechanical strength and creep resistance at elevated temperature by viscous flow mechanisms.

Between about 1100 and 1200°C the nanometre-sized γ-Al_2O_3 + SiO_2 phase assemblage transforms to mullite. The phase transformation is associated with a strong increase of mean grain size and leads to a distinct reduction of tensile strength. Heat treatments of Nextel 440 fibres between 1200 and 1400°C cause a drastic decrease in strength, attributed to grain coarsening. According to the reciprocal relationship between grain size and strength:[7]

$$\sigma \propto d^{-p}$$

(where σ is strength, d is grain size and $p \approx 0{\cdot}5$), it turns out that the coarsening of small grains in particular has a strong influence on strength. A strength reduction of 23% (380 MPa) is estimated considering Nextel grain growth data between 1200 and 1400°C. The slightly higher strength loss of 31% (520 MPa) found experimentally may be caused by changes in grain morphology. Strong agglomerations of micropores or glassy phase are assumed if the irregular-shaped mullite crystals develop planar interfaces at high temperature. Obviously the increasing flaw density reduces the mechanical strength.

Above 1550°C exaggerated grain growth takes place in Nextel 440 fibres. Presumably secondary grain growth is assisted by the existence of grain boundary glassy phase separating the surfaces of the small and large grains.[8] Low viscosity glassy phase occurring at high temperature is related with the B_2O_3 content of the fibres. Retention of B_2O_3 in fired Nextel 440 fibres is deduced from very small weight loss (< 1%) after heat treatment at 1600°C.[1]

As-received Altex 2K fibres exhibit similar microstructures to Nextel 440 fibres in the temperature range just beyond the γ-Al_2O_3 + SiO_2 to mullite transformation (1200°C). We assume therefore that the Altex fibres were produced in this temperature range. This suggestion fits well with the observation that there is no significant change of the microstructure up to 1200°C. Moreover, no glassy phase is detected, probably due to the lack of B_2O_3 flux in Altex 2K fibres. The probable lack of a grain boundary glass phase accounts for the better creep resistance of Altex 2K fibres than of Nextel 440, although the room temperature strength of Altex 2K is comparatively low. The increase of tensile strength of Altex 2K fibres after annealing at 1000°C is attributed to the reduction of residual stresses. Residual stresses may be caused by rapid cooling of the fibres during the fabrication process, due to anisotropy of the thermal expansion coefficients of mullite (~3·9 $\times 10^{-6}$ K^{-1} || a-axis and ~7 $\times 10^{-6}$ K^{-1} || b-axis)[9].

The present study of the two commercial polycrystalline aluminosilicate fibres with near-stoichiometric mullite composition shows that fibres consisting of nanocrystalline γ-Al_2O_3 + SiO_2 in the as-received state are suitable for high strength applications at low or moderate temperatures. For applications at higher temperatures (> 1100°C), fibres consisting of polycrystalline mullite without any coexisting glass phase will be more favourable due to the higher creep resistance and resistance against creep-induced fracture.

Moreover, it has been shown that suitable mechanical properties for high temperature applications of the fibres demand homogeneous and extremely fine-grained microstructures and that the content of non-crystalline grain boundary phase should be as low as possible. However, fulfilment of both requirements simultaneously is difficult. For instance, addition of B_2O_3 to a diphasic aluminosilicate starting material causes high nucleation density of mullite, leading to a favourable fine-grained microstructure.[4] On the other hand, due to B_2O_3 addition, the tendency of forming amorphous grain boundary phases is increased which has a negative influence on the high temperature mechanical properties.

Another result of the investigation is that grain coarsening at elevated temperatures does reduce the strength of the fibres drastically. Therefore further developments of mullite fibre should have the aim of grain growth reduction. A possible way to be successful is doping the starting materials with vanadium or chromium, both of which have a negative influence on the mullite grain growth rate.[10]

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