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Synthesis of α-alumina fibre from modified aluminium alkoxide precursor

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Polycrystalline alumina fibre was successfully synthesized by pyrolysis of a preceramic fibre formed from aluminium compounds with alkoxy and chelate ligands. A mixture of ethyl 3-oxobutanoatodiisopropoxyaluminium (EOPA) and tri-sec-butoxyaluminium (SBA) was reacted with glacial acetic acid yielding a polymeric product. The IR absorptions at 630 and 700 cm^{-1} due to the Al–O bond changed from sharp to broad bands by treatment with acetic acid. The ^{27}Al resonance at 35 p.p.m. increased in intensity when EOPA–SBA (7/3) was treated with 30 mol % acetic acid. An increase in the EOPA to SBA ratio 5/5 to 9/1 also raised the intensity of the signal at 35 p.p.m. The viscosity of the polymeric product increased in intensity as the amount of acetic acid increased. The viscosity of precursor increased with increasing the ratio of EOPA to SBA, and decreased with increasing measurement temperature from 45 to 75 °C. The precursor polymer pyrolysed at 500 °C in air was amorphous to X-rays, and crystallized in γ-alumina at 840 °C. The precursor fibres were pyrolysed to yield fine-grained fibres of α-alumina at 1200 °C for 1 h.

1. Introduction

Ceramic fibres have increasing applications for the reinforcement of metals and ceramics. Alumina and modified alumina fibres are used for temperature resistant fibres.

A sol process has been used for the synthesis of a ceramic fibre precursor, since refractory oxides have extremely high melting points as well as the low viscosity of melts. Alumina and silica–alumina fibres have been fabricated using the sol process. Various aluminium compounds, such as aluminium salts [1–4] and alkoxides [5, 6] are hydrolysed, and then condensed and/or polymerized until an appropriate viscosity for spinning was reached. The time-dependent viscosity of sol, however, makes the spinning condition critical. The viscosity increases very rapidly once the formation of cross-linkage starts. The organic additives are, therefore, used to raise the viscosity of the solutions and to improve the spinning characteristics.

On the other hand, the time-independent viscosity of the starting polymer in the polymer route is one of the most marked differences from the sol–gel process. Yogo [7] demonstrated the synthesis of zirconia fibre from the precursor with stable viscosity.

This paper describes the synthesis of alumina fibre from a mixture of aluminium chelate compound and alkoxide. The polymeric precursor was synthesized by the reaction of ethyl 3-oxobutanoatodiisopropoxyaluminium with tri-sec-butoxyaluminium in the presence of glacial acetic acid. The former has a bidentate ligand, whereas the latter contains three monodentate ligands bonded to aluminium. Several precursors were synthesized from a mixture of two aluminium compounds. The relations between the structure of precursor and the viscosity were investigated. Crack-free α-alumina fibres were prepared from the polymer fibres, which were spun from the polymeric aluminium precursor.

2. Experimental procedure

2.1. Starting materials

Ethyl 3-oxobutanoato-diisopropoxy aluminium ($Al(O^iC_3H_7)_2(CH_3COCHCOOC_2H_5)$, EOPA) was prepared according to Patterson *et al.* [8]. Tri-sec-butoxyaluminium (aluminium sec-butoxide, $Al(O^{sec}C_4H_9)_3$, SBA) was commercially available.

2.2. Synthesis of alumina

The following procedure for the synthesis of Al_2O_3 is representative. The procedure for the synthesis of precursor was carried out under nitrogen without any solvent.

1.08 g of glacial acetic acid (18.0 mmol) was added dropwise to a mixture of 14.8 g of ethyl 3-oxobutanoatodiisopropoxyaluminium (54.0 mmol) and 1.51 g of tri-sec-butoxyaluminium (6.13 mmol), and then the reaction mixture was refluxed at 190 °C for 2 h to give a pale yellow transparent liquid. Volatile components were removed from the reaction product *in vacuo* yielding a viscous liquid.

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The resultant product was pyrolysed in air from room temperature to 500 °C at 1 °C min^{-1}. The pyrolysis product was heat treated at temperatures between 800 and 1200 °C for 1 h.

The precursor was melt in the brass extruder above 100 °C and then extruded through the spinneret with a diameter of 300 μm below 60 °C. The polymer fibre was dried at room temperature, and then fired from room temperature to 600 °C at 0.2 °C min^{-1} in air. The ceramic fibre was subsequently heat treated at temperatures from 800 to 1200 °C for 1 h.

2.3. Characterization of products

The organic product was characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectra. IR spectra of products were measured by the liquid film method. ^{13}C NMR spectra were measured in $CDCl_3$ solution using tetramethylsilane as an internal standard. ^{27}Al NMR spectra were measured at 65.18 MHz using a Bruker 250 AC spectrometer. The spectra were recorded in $CDCl_3$ solution with $Al(H_2O)_6^{3+}$ as an external standard. The volatile components as reaction by-products were analysed by GC (gas chromatography). Molecular weights were determined cryoscopically using benzene as a solvent, and with field desorption mass spectroscopy (FD MS). The molecular structure was analysed by fast atom bombardment mass spectroscopy (FAB MS). The viscosity of the polymer was measured by a rotational viscometer using a cone-and-plate and a spindle, respectively, depending upon the magnitude of viscosity, from 45 to 75 °C. The burn-out and crystallization behaviour of polymeric precursor were measured with DTA–TG at a heating rate of 10 °C min^{-1}.

The pyrolysis product was analysed by X-ray diffraction analysis (XRD) with CuK_α radiation and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Synthesis and characterization of a polymeric aluminium chelate compound

3.1.1. Synthesis of a polymeric aluminium chelate compound

A mixture of ethyl 3-oxo-butanoatodiisopropoxyaluminium (EOPA) and tri-sec-butoxyaluminium (SBA) was reacted with glacial acetic acid (AcOH) affording precursors for alumina. No water was used for the synthesis of precursors in order to prevent the gelation of products.

The polymeric product synthesized from EOPA–SBA and acetic acid was a transparent, viscous liquid and soluble in usual organic solvents, such as benzene and chloroform.

3.1.2. IR spectroscopy

The IR spectra of starting EOPA–SBA (molar ratio, 7/3) and reaction product with 30 mol % acetic acid are shown in Fig. 1. The absorption bands of the Al–O bond at 630 and 700 cm^{-1} [9, 10] in the starting EOPA–SBA (Fig. 1a) changed from separate to coalesced bands after polymerization as shown in Fig. 1b. This change suggests the formation of the product with various kinds of Al–O bonds from the starting compound. The absorption bands ascribed to ethyl 3-oxo-butanoato ligands at 1620, 1570 and 1530 cm^{-1} [10] were observed in both compounds.

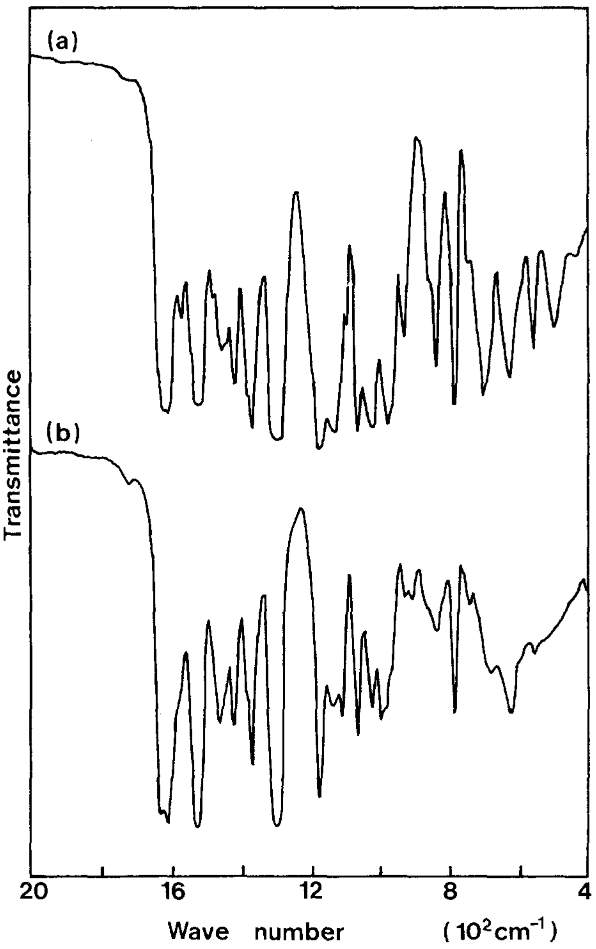


Figure 1 Infrared spectra of starting aluminium compound and polymeric product. (a) A mixture of EOPA and SBA (7/3). (b) Polymeric product from EOPA-SBA (7/3) with 30 mol % acetic acid.

3.1.3. ^{27}Al NMR spectroscopy

The ^{27}Al NMR spectrum of the polymeric precursor formed from EOPA and SBA was measured in order to investigate the coordination of aluminium atom.

The spectrum of the mixture of EOPA and SBA (7/3) is compared with that of reaction products with 30 mol % acetic acid in Fig. 2. The signals centred at 62 and 4.2 p.p.m. in Fig. 2a are assigned to the four- and six-coordinated aluminium, respectively [11–13]. The presence of six-coordinated aluminium shows the association of starting EOPA–SBA in $CDCl_3$ solution.

The signal assigned to four-coordinated aluminium in the mixture of EOPA–SBA decreased in intensity with the treatment of acetic acid as shown in Fig. 2b. Also, the signal centred at 35 p.p.m. appeared after the treatment with 30 mol % acetic acid. The coordination number of aluminium is reported to increase from 4 to 6 as the chemical shift approaches to 0 p.p.m.

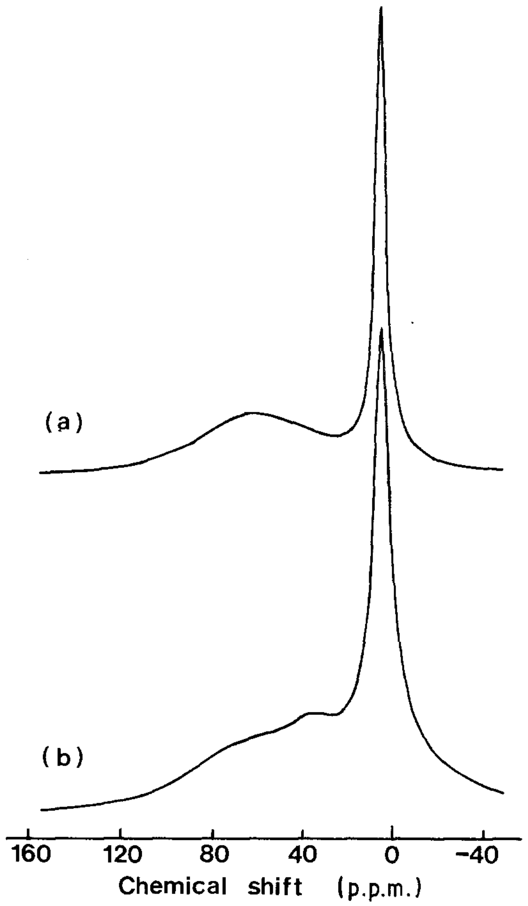


Figure 2 Change of ^{27}Al NMR spectra of EOPA–SBA with the treatment of acetic acid. (a) A mixture of EOPA–SBA (7/3). (b) Product formed from EOPA–SBA (7/3) and 30 mol % AcOH.

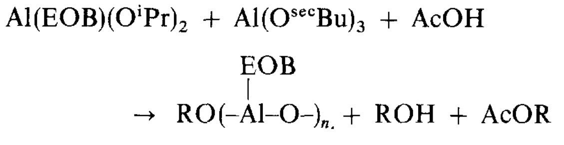
[11–13]. The new signal can be assigned tentatively to penta-coordinated aluminium [14]. The steric environment around aluminium atom changed, therefore, to be more crowded to afford higher coordination number than that in the starting EOPA–SBA.

Mixtures of EOPA and SBA with various ratios were treated with 30 mol % acetic acid, and their spectra are shown in Fig. 3. The signal at 35 p.p.m. increased in intensity with increasing ratio of EOPA to SBA from 3/7 (Fig. 3d) to 9/1 (Fig. 3a) in the starting mixture. EOPA has a bidentate ligand of ethyl 3-oxobutanoato (EOB), which is bonded to aluminium using two carbonyl oxygens. The larger amount of EOPA, therefore, increases, the amount of the coordination number of aluminium from four to five and/or six.

On the basis of these results, not only the treatment of acetic acid but also the ratio of EOPA to SBA vary the coordination environment of aluminium in a precursor.

3.1.4. GC analysis of distillates

The reaction between aluminium compounds and acetic acid is considered to proceed as shown in Equation 1. Alkoxy groups on the aluminium atom are eliminated by the reaction with acetic acid



$$\mathrm{Al(EOB)(O^{i}Pr)_2 + Al(O^{sec}Bu)_3 + AcOH} \rightarrow \mathrm{RO(\text{-}\overset{\overset{\displaystyle EOB}{|}}{Al}\text{-}O\text{-})_{n} + ROH + AcOR} \quad (1)$$

The formation of isopropyl alcohol (R = ^{i}Pr), sec-butyl alcohol (R = ^{sec}Bu), isopropyl acetate (AcO^{i}Pr) and sec-butyl acetate (AcO^{sec}Bu) as low boiling components was confirmed by ^{13}C NMR and GC.

The distillates from various mixtures of EOPA–SBA and 30 mol % AcOH were analysed by GC. Fig. 4 correlates the ratio of EOPA over (EOPA + SBA) in the starting materials to the ratio of isopropyl over (isopropyl + sec-butyl) groups in the distillates. The ratio of distillate is corrected on the basis of number of alkoxy groups on each aluminium compound, since EOPA and SBA have two and three alkoxy groups, respectively. The distillates are the mixtures of alcohol and its acetate. The ratio of isopropyl to sec-butyl group in the starting compounds has a linear relationship with the ratio of distillates. Acetic acid eliminates isopropoxy and sec-butoxy ligands from EOPA and SBA, respectively, regardless of the ratio of EOPA to SBA. The fraction of isopropyl group in distillates is lower than that in the starting mixture. The isopropyl group on EOPA is, therefore, less reactive to acetic acid than the sec-butyl group on SBA.

3.1.5. Molecular weight

The molecular weight of reaction products from EOPA–SBA–30 mol % AcOH was measured cryoscopically in benzene. The calculated molecular weights of starting EOPA and SBA are 274.3 and 246.3, respectively. The molecular weight of polymeric products increased from 500 to 800 as the EOPA to SBA ratio increased from 0/10 to 9/1.

The precursor formed from EOPA–SBA (9/1) with 30 mol % acetic acid was analysed by FD MS. The precursor had the distribution of molecular ion peaks below 1000. The *m/e* (mass/electric charge) peaks appeared at around 400 and 600.

3.1.6. Structure of polymeric product

The polymeric product has ethyl 3-oxobutanoato (EOB) ligands on the basis of IR spectroscopy. ^{27}Al NMR spectra show the precursor comprises six-coordinated aluminium–oxygen octahedra. Since EOB is a bidentate ligand having two coordination oxygens, a structure unit of $(\text{-Al(EOB)}_2\text{-O-})_n$ is considered to constitute the aluminium–oxygen octahedra. The FAB MS of precursor formed from EOPA–SBA (9/1)–30 mol % acetic acid also showed the fragment at 300, which suggests the presence of $(\text{-Al(EOB)}_2\text{-O-})$ moiety. The measurement of molecular weight, however, reveals that the degree of polymerization (n) is below three. A mixture of $(\mathrm{RO})_{3-n}\mathrm{Al(EOB)}_n$ ($n < 3$) appears to constitute the low molecular weight components less than 500. The polymeric product consists mainly of monomeric chelate compounds and their oligomers.

3.2. Viscosity and spinnability of precursor

The product formed from EOPA–SBA and glacial acetic acid had a time-independent and stable viscosity.

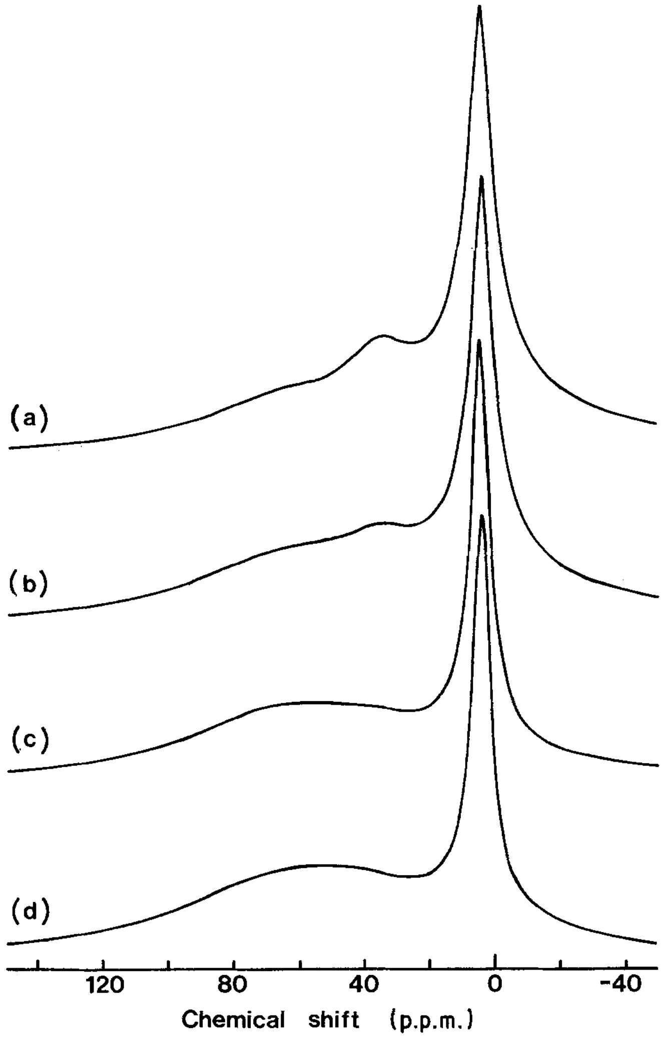


Figure 3 Change of ^{27}Al NMR spectra of polymeric precursor with the ratio of EOPA to SBA. (a) EOPA–SBA (9/1) with 30 mol % AcOH, (b) EOPA–SBA (7/3) with 30 mol % AcOH, (c) EOPA–SBA (5/5) with 30 mol% AcOH, (d) EOPA–SBA (3/7) with 30% AcOH.

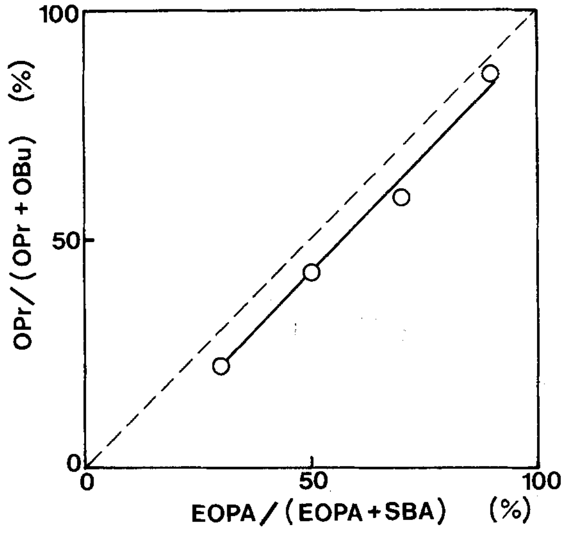


Figure 4 Change of the ratio of isopropoxy to sec-butoxy groups in distillates with EOPA–SBA in the presence of 30 mol % acetic acid.

The viscosities of polymeric precursors formed from EOPA–SBA and 30 mol % of acetic acid are shown in Fig. 5. The viscosity increased with increasing ratio of EOPA to SBA from 5/5 to 9/1. Since EOPA gives more highly coordinated aluminium than SBA, the viscosity of precursor depends on the amount of chelate ligands in the precursor. The increase in viscosity corresponds to the increased amount of pentacoordinated aluminium atom as shown in Fig. 3.

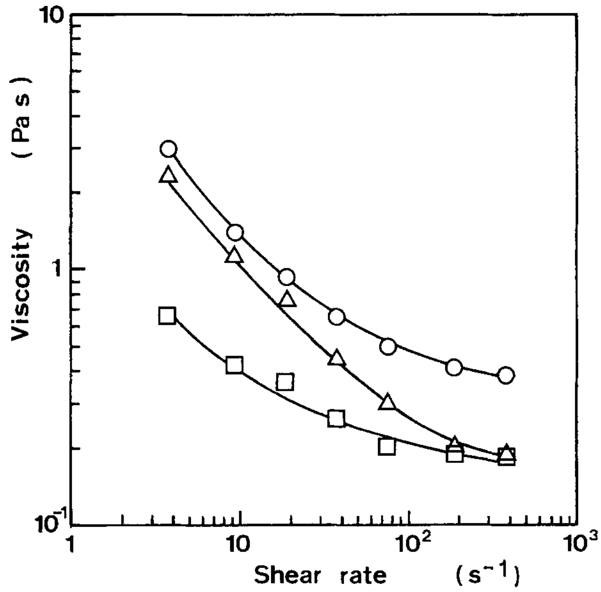


Figure 5 Change of viscosity for precursor formed from EOPA–SBA with shear rate at 75 °C. (○ EOPA–SBA = 9/1, △ EOPA–SBA = 7/3, □ EOPA–SBA = 5/5)

Since the viscosity of the precursor decreases with the shear rate, the precursor is non-Newtonian. The distribution of molecular weight is responsible for the non-Newtonian behaviour of the precursor.

The variation of viscosity with measurement temperature at a shear rate of 9.6 s^{-1} is shown in

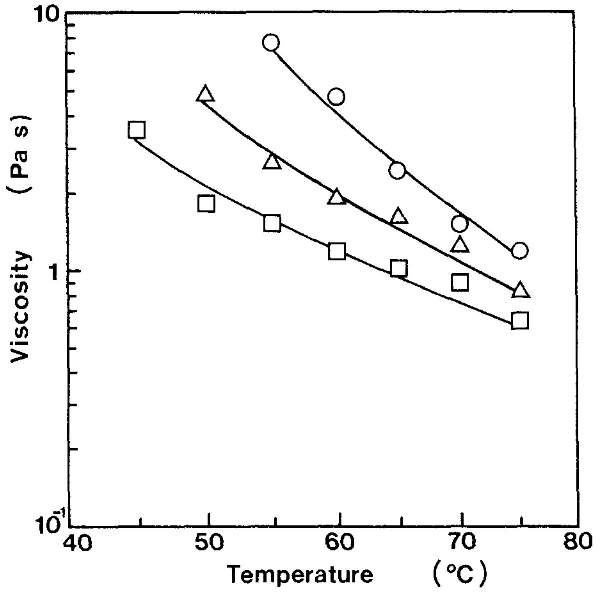


Figure 6 Variation of viscosity for precursor with the measurement temperature from 45 to 75 °C at shear rate of 9.6 s^{-1}. (○ EOPA–SBA = 9/1, △ EOPA–SBA = 7/3, □ EOPA–SBA = 5/5).

Fig. 6. The viscosity of the precursor formed from EOPA–SBA and 30 mol % acetic acid decreased with increasing measurement temperature from 45 to 75 °C. The precursor from EOPA to SBA (9/1) decreased in magnitude of viscosity from 7.78 Pa s (77.8 poise) to 1.21 Pa s (121 poise) with increasing measurement temperature from 55 to 75 °C. Similar to Fig. 5, the higher amount of EOPA in a precursor showed the higher value of viscosity.

The precursor formed from EOPA–SBA (9/1) and 30 mol % acetic acid was extruded through a spinneret into a fibre. The working temperature was from 40 to 50 °C. The length of precursor fibre ranged from 50 to 80 cm. The viscosity suitable for extrusion was found to be from 1 to 10 Pa s.

3.3. Synthesis of alumina from an aluminium chelate precursor

3.3.1. Crystallization behaviour

The TG analysis of polymeric product formed from EOPA–SBA and 30 mol % acetic acid showed the conversion yield of ceramic was 23% in weight. The exothermic peak at 840 °C on heating in the DTA analysis is due to the crystallization of γ-alumina.

The pyrolysed product at 500 °C was amorphous to X-rays, and began to crystallize in γ-alumina after heat treatment at 800 °C for 1 h. The XRD analysis showed that α-alumina began to form around 950 °C. The mixture of α- and γ-phase was produced after heat treatment at 1100 °C for 1 h. Only highly crystalline α-alumina was obtained at 1200 °C for 1 h.

3.3.2. Conversion of polymer fibre to ceramic fibre

Polymer fibres were spun from the aluminium chelate precursor around 50 °C, and then fired in air above 800 °C.

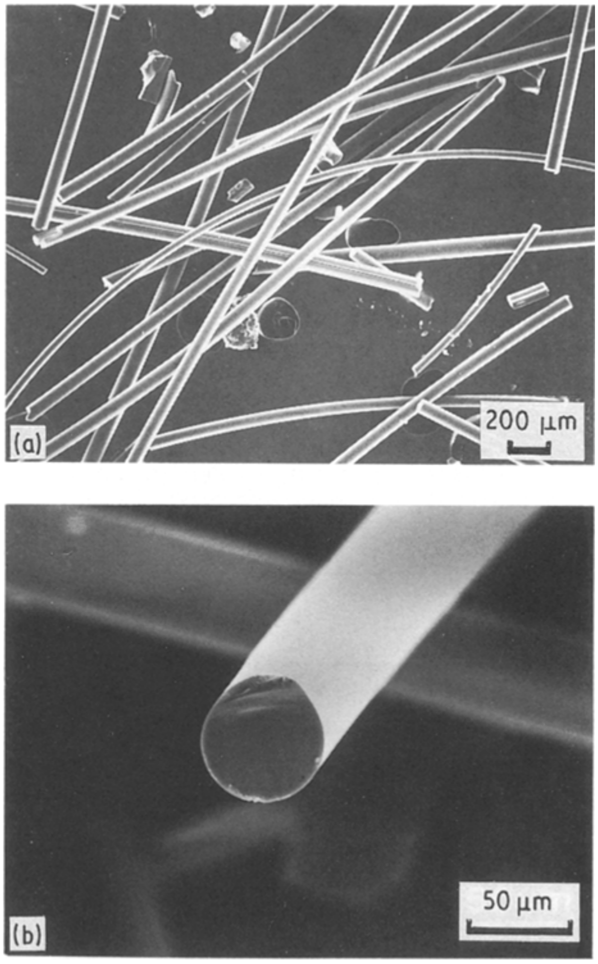


Figure 7 SEM pictures of alumina fibres: (a) 1200 °C for 1 h (b) Fracture surface of (a).

Alumina fibres synthesized from the polymer fibre at 1200 °C for 1 h are shown in Fig. 7. The disruption-free fibres were synthesized from the precursor fibre as shown in Fig. 7a. The diameter of the fibre ranged from 30 to 100 µm. The cross-section of fibre shown in Fig. 7b is circular, and has a quite small grain size. The fracture surface contains no pores, and shows the fibre is practically fully dense.

4. Conclusions

Alumina fibre was synthesized successfully from aluminium chelate precursor without any additives of polymer for the adjustment of viscosity. The results are summarized as follows.

1. A mixture of ethyl 3-oxobutanoatodiisopropoxyaluminium and tri-sec-butoxyaluminium was reacted with glacial acetic acid yielding the viscous precursor for alumina fibre.
2. The polymeric product was a mixture of chelate compounds and oligomers, and had a molecular weight below 1000.
3. The increased amount of ethyl 3-oxobutanoato ligand resulted in the increased content of higher coordination number for aluminium, which led to the increase in viscosity of precursor for alumina.
4. The viscosity of the bulk polymer was independent of time, and was controlled by the selection of

temperature in order to obtain the appropriate viscosity for spinning.

5. The preceramic fibre melt-spun from the polymer was converted to α-alumina fibre with uniform and fine grain size after heat treatment at 1200 °C.

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