

Synthesis of polycrystalline alumina–zirconia fibre using chelated aluminium–zirconium precursor

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Polycrystalline alumina–zirconia fibres were successfully synthesized by pyrolysis of preceramic fibres formed from mixed aluminium–zirconium chelate compounds. Ethyl 3-oxobutanoatodiisopropoxyaluminium (EOPA) was reacted with zirconium tetrabutoxide (TBZ) in the presence of glacial acetic acid yielding a polymeric product. The infrared absorptions from 500–625 cm^{-1} due to Al–O and Zr–O bonds changed from sharp to coalesced bands by treatment with acetic acid. The signal at 40 p.p.m. in the ^{27}Al spectra of EOPA–TBZ increased in intensity on treating with acetic acid. The viscosity of the polymeric product increased as the amount of acetic acid increased. The viscosity of the precursor decreased on increasing the measurement temperature from 60 °C to 75 °C. The precursor polymer pyrolysed at 800 °C in air showed a broad X-ray diffraction of γ -alumina, and crystallized in a mixture of γ -alumina and tetragonal zirconia at 1000 °C. The median diameter of tetragonal zirconia in the α -alumina matrix was 33 nm, when EOPA–TBZ (Al/Zr = 9/1) was heat treated at 1300 °C for 1 h. The precursor fibres were pyrolysed at 1300 °C to yield fine-grained fibres of α -alumina including tetragonal zirconia, which was confirmed by Raman microprobe spectroscopy.

1. Introduction

Modified alumina fibres are temperature-resistant fibres, and have various applications in composites with metals and ceramics. Alumina–zirconia fibre has been reported to have improved high-temperature properties compared to alumina fibre [1]. The fine dispersion of tetragonal zirconia has been reported to contribute to the higher strength of alumina–zirconia fibre [1–3].

Alumina and modified alumina fibre have been fabricated via the solution technique including a sol–gel process, because refractory oxides have extremely high melting points as well as the low viscosity of melts. The precursor fibre was spun from a viscous sol prepared by the hydrolysis of aluminium compounds, such as aluminium acetate [4, 5], oxychloride [6] and alkoxide [7, 8]. The aqueous solution containing aluminium compounds was condensed and/or polymerized until an appropriate viscosity for spinning was reached. However, the viscosity of a sol is time-dependent, and changes very rapidly once the formation of cross-linkage starts, yielding unspinnable gels. The control of viscosity, therefore, is critical to establish the spinning conditions of the sols.

On the other hand, the advantage of the polymer route to the preceramic fibre is the stable viscosity of the starting polymer, which is one of the most distinct differences from the sol–gel process. Yogo and Iwahara synthesized alumina fibres from chelated [9] and modified aluminium alkoxide precursor [10], which have a time-independent and stable viscosity.

The present paper describes the synthesis of alumina–zirconia fibre from aluminium–zirconium chelate precursor. The polymeric precursor was synthesized by the reaction of aluminium chelate compound with zirconium tetrabutoxide in the presence of glacial acetic acid. The polymeric precursor was analysed by infrared and ^{27}Al NMR spectroscopy. The viscosity of polymer was investigated using a rotational viscometer. Crack-free alumina fibres dispersed with tetragonal zirconia were prepared from the polymer fibres, which were spun from the polymeric aluminium–zirconium chelate precursor.

2. Experimental procedure

2.1. Starting materials

Ethyl 3-oxobutanoatodiisopropoxyaluminium($(\text{CH}_3\text{COCHCOOC}_2\text{H}_5)_2\text{Al}(\text{O}^i\text{Pr})_2$, EOPA) was prepared as described by Patterson *et al.* [11]. Zirconium tetrabutoxide ($\text{Zr}(\text{OBu})_4$, tetrabutoxyzirconium, TBZ) was commercially available.

2.2. Synthesis of alumina–zirconia

The following procedure for the synthesis of Al_2O_3 –18.2 mol% ZrO_2 (molar ratio of Al/Zr = 9/1) is representative. The procedure was carried out under nitrogen without any solvent.

A mixture of ethyl 3-oxobutanoatodiisopropoxyaluminium (6.97 g, 25.4 mmol) and zirconium tetrabutoxide (1.08 g, 2.81 mmol, Al/Zr = 9/1) was heated

at 90 °C for 1 h to give a transparent solution. Glacial acetic acid (0.510 g, 8.49 mmol, 30 mol % for the total amounts of aluminium and zirconium) was added dropwise to the reaction mixture at room temperature. Then, the reaction mixture was refluxed for 2 h to give a pale yellow transparent solution. Volatile components were removed from the solution *in vacuo* yielding a yellow oil. 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 1300 °C for 1 h.

The precursor fibre was spun from the bulk polymer using a glass rod. Also, the precursor was melted in a brass extruder above 80 °C, and extruded through the spinneret with a diameter of 300 µm below 60 °C. The polymer fibre was dried at room temperature, and was then fired from room temperature to 800 °C at 0.2 °C min⁻¹ in air. The ceramic fibre was subsequently heat treated at 1300 °C for 1–6 h.

2.3. Characterization of products

The organic product was characterized using infrared (IR) and nuclear magnetic resonance (NMR) spectra. IR spectra of polymers were measured by the liquid film method. ¹H and ¹³C NMR spectra were measured in CDCl₃ solution using tetramethylsilane as an internal standard. ²⁷Al NMR spectra were measured

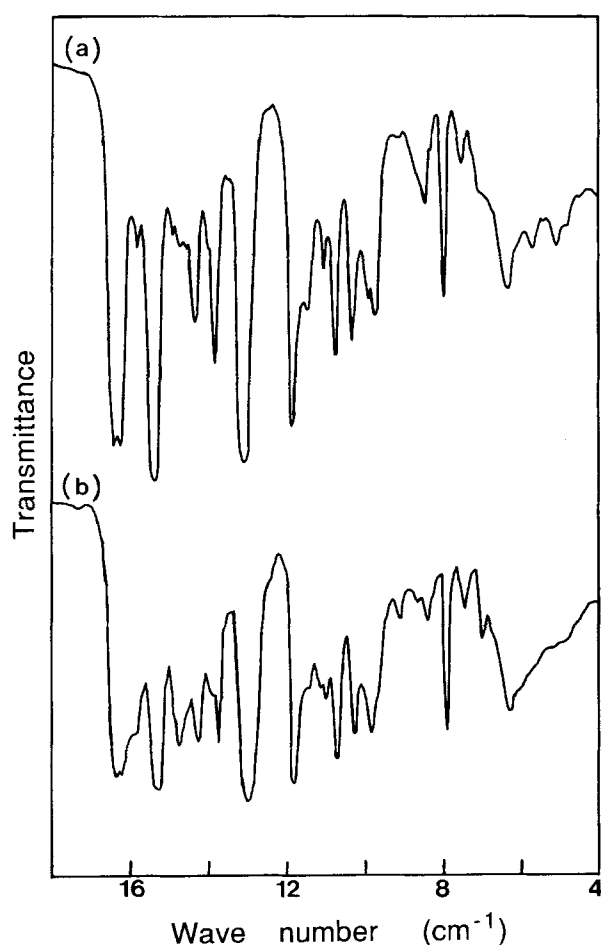


Figure 1 IR spectra of starting EOPA-TBZ (Al/Zr = 7/3) and reaction product with 30 mol % AcOH: (a) starting EOPA-TBZ; (b) polymeric product formed from EOPA-TBZ.

at 65.18 MHz in CDCl₃ solution with Al(H₂O)₆³⁺ as an external standard. Molecular weights were determined cryoscopically using benzene as a solvent. The volatile components collected in a chilled trap were analysed by gas chromatography (GC). The viscosity of the polymer was measured by a rotational viscometer using a cone-and-plate from 40–80 °C.

The pyrolysis product was analysed by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The amount of tetragonal phase was analysed based upon the intensity of (111)_t, (111)_m, and (111̄)_m reflections as reported [12]. The ceramic fibre was characterized using scanning electron microscopy (SEM) and Raman microprobe analysis.

3. Results and discussion

3.1. Synthesis and characterization of polymeric aluminium–zirconium precursor

3.1.1. Synthesis of polymeric aluminium–zirconium precursor

The aluminium chelate compound (EOPA) was reacted with zirconium butoxide (TBZ) in the presence of glacial acetic acid (AcOH) affording precursors for alumina–zirconia. No water was used for the reaction in order to avoid the gelation, which led to the rapid increase of viscosity losing spinnability.

The polymeric product synthesized from EOPA and TBZ was a viscous liquid and soluble in the usual organic solvents, such as benzene and chloroform.

3.1.2. IR spectroscopy

The IR spectra of the starting EOPA–TBZ (Al/Zr = 7/3) and polymer are shown in Fig. 1. The absorption bands of Al–O and Zr–O bonds appear at 625 and from 500–560 cm⁻¹, respectively [13, 14]. These absorptions changed from separate to coalesced bands after polymerization. This change suggests the formation of the product with various kinds of Al–O and Zr–O bonds from the starting compound. The absorption bands ascribed to ethyl 3-oxobutanonate (EOB) ligands at 1570, 1520 and 1300 cm⁻¹ [14], were observed in both compounds.

3.1.3. ²⁷Al NMR spectroscopy

Fig. 2 shows the ²⁷Al NMR spectra of starting EOPA–TBZ (9/1) and its reaction products with acetic acid.

The starting mixture shows three signals centred at 5.1, 37 and 60 p.p.m. as shown in Fig. 2a. These signals are assigned to 6-, 5- and 4-coordinated aluminium, respectively [15–18]. A monomeric EOPA itself is 4-coordinated, because EOB is a bidentate ligand, which has two carbonyl oxygens coordinating to a metal atom. The 5- and 6-coordination of aluminium result from various associations between aluminium–alkoxy and aluminium–chelate (EOB) species in CDCl₃ solution, as reported for aluminium alkoxides [16].

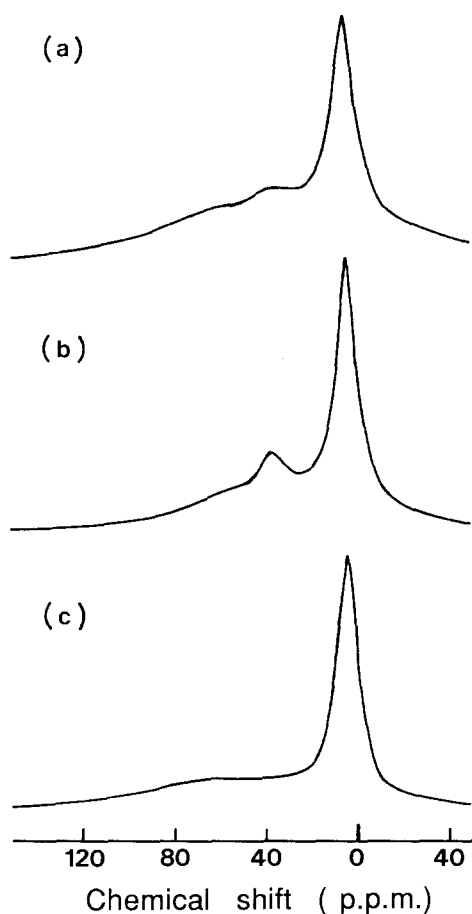
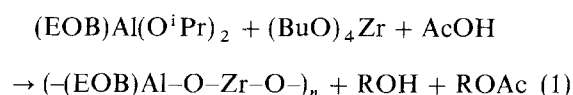


Figure 2 Change of ^{27}Al NMR spectra of EOPA-TBZ with amounts of acetic acid: (a) starting EOPA-TBZ (Al/Zr = 9/1); (b) product formed with 30 mol% AcOH; (c) product formed with 70 mol% AcOH.

The signal due to 4-coordination decreased in intensity on treatment with acetic acid, while the resonance of 5-coordinated aluminium at 40 p.p.m. increased in intensity through treatment with acetic acid (Fig. 2b). When 70 mol% acetic acid was used, the product contained exclusively octahedrally coordinated aluminium with a small amount of tetrahedrally coordinated aluminium as shown in Fig. 2c. The starting EOPA-TBZ undergoes a change of coordination around aluminium, which reflects the reaction of EOPA-TBZ with acetic acid yielding aluminium-zirconium precursors.

3.1.4. Gas chromatography analysis of volatile organics

The reaction between aluminium, zirconium compound and acetic acid gave the reaction product composed of the Al-Zr precursor and volatile components. The volatiles were confirmed to consist of isopropyl alcohol ($^i\text{PrOH}$), butyl alcohol (BuOH), iso-propyl acetate ($^i\text{PrOAc}$) and butyl acetate (BuOAc), by gas chromatography (GC) and ^{13}C NMR. The reaction, thus, is considered to proceed as shown in Equation 1 ($\text{R} = ^i\text{Pr}$ and Bu).



The volatiles from various mixtures of EOPA-TBZ and 30 mol% acetic acid were analysed by GC. The ratio of TBZ to EOPA + TBZ in the starting materials is plotted against the ratio of butoxy to iso-propoxy + butoxy groups in the low-boiling components in Fig. 3. The ratio of volatiles is corrected on the basis of the number of alkoxy groups on each aluminium and zirconium compound, because EOPA and TBZ have two and four alkoxy groups, respectively. Acetic acid eliminates iso-propoxy and butoxy ligands from EOPA and TBZ, respectively. The fraction of butoxy groups increases with increasing ratio of TBZ(Zr) to EOPA(Al) in the starting compound. The percentage of butoxy groups in the low-boiling products is lower than that in the starting mixture. The butoxy group on TBZ is, therefore, less reactive to acetic acid than the iso-propoxy group on EOPA.

The amount of alkoxy groups collected as low-boiling products is about 60% of the total alkoxy groups in a starting EOPA-TBZ (9/1)-30 mol% AcOH. About 40% of the alkoxy groups remains to be bonded to the aluminium and zirconium in the polymeric product. The ^{13}C NMR spectrum also revealed the presence of alkoxy groups in the polymeric product.

3.1.5. Molecular weight

The calculated molecular weights of EOPA and TBZ are 274.3 and 383.7, respectively. The molecular weight of the starting EOPA-TBZ (9/1) was 445 (calculated for EOPA-TBZ (Al/Zr = 9/1), 285.2) with cryoscopic measurements in benzene. This result shows the starting EOPA-TBZ associates yielding equilibria between dimers and monomers. On the other hand, the molecular weight of the polymeric product increased from 640 to 780 with increasing acetic acid in amount from 10 mol% to 30 mol%.

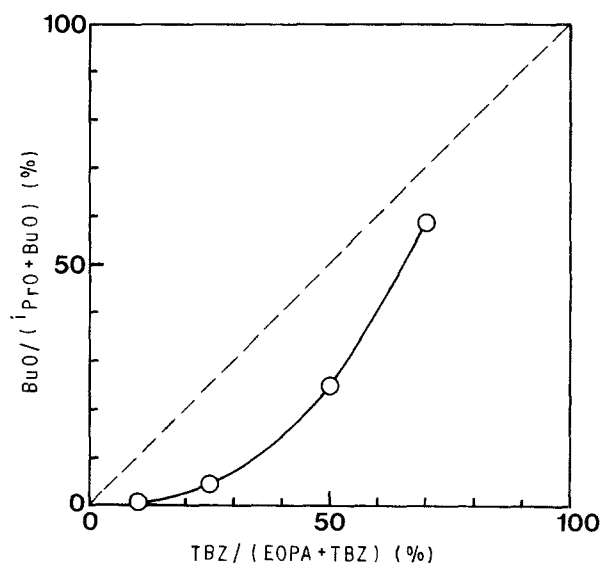


Figure 3 Change of the ratio of butoxy to iso-propoxy group in volatiles with TBZ over EOPA + TBZ in the presence of 30 mol% AcOH.

3.1.6. Structure of the polymeric product

The polymeric product has ethyl 3-oxobutanoate (EOB) ligands shown by IR spectroscopy in Fig. 1. The oligomer in the polymeric product has a structure unit of $-\text{Al}(\text{EOB})_2-\text{O}-$ including 6-coordinated aluminium, because EOB is a bidentate ligand. The structure of $-\text{Al}(\text{OR})(\text{EOB})-\text{O}-$ could constitute 5-coordinated aluminium, because alkoxy groups are bonded to metals in the polymeric product as shown in Section 3.1.4. The polymeric product consists mainly of oligomeric chelate compounds.

3.2. Viscosity and spinnability of the polymer

The changes in viscosities at 70 °C with shear rate for starting EOPA-TBZ (Al/Zr = 9/1) and EOPA-TBZ-AcOH are shown in Fig. 4. The viscosity below 0.1 Pa s for the starting EOPA-TBZ was too low to spin fibres. The viscosity of the precursor increased on increasing amount of acetic acid from 20 mol % to 40 mol %. The viscosity of the precursor decreased with shear rate at 70 °C.

The variations of viscosity, η , with measurement temperature at a shear rate of 1.92 s^{-1} are shown in Fig. 5. The viscosity of the precursor formed from EOPA-TBZ (Al/Zr = 9/1)–30 mol % AcOH was extremely high at room temperature, and decreased in magnitude from 14.0 Pa s (140 P) to 3.58 Pa s (35.8 P) on increasing the measurement temperature from 60 °C to 75 °C.

The viscosity can, therefore, be controlled by the amount of acetic acid as well as the working temperature. The viscosity suitable for extrusion was found

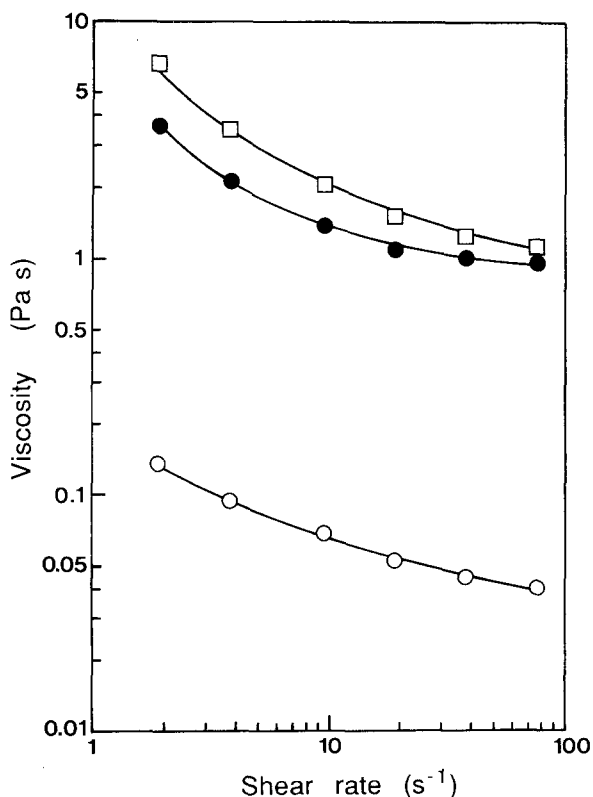


Figure 4 Change of viscosity, η with shear rate at 70 °C for EOPA-TBZ (Al/Zr = 9/1) treated with various amounts of acetic acid: (○) no acid; (●) 20 mol %; (□) 30 mol %.

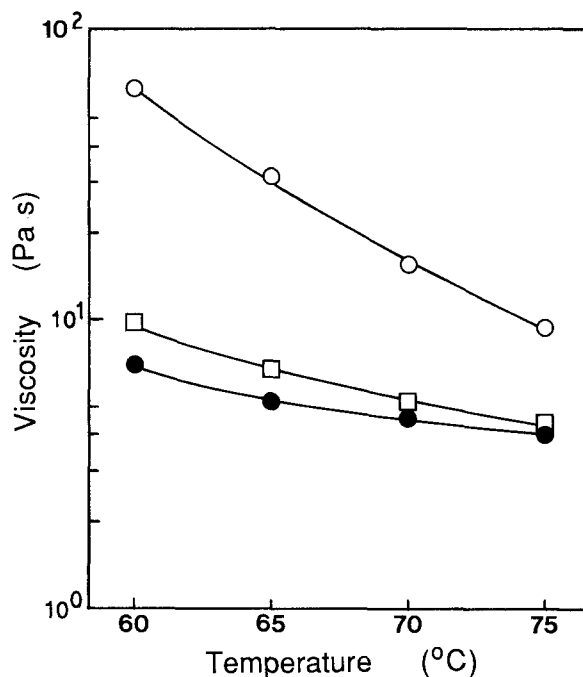


Figure 5 Variation of viscosity, η , with measurement temperature from 60–75 °C at shear rate of 1.92 s^{-1} for precursors synthesized from EOPA-TBZ (Al/Zr = 9/1) in the presence of various amounts of acetic acids: (●) 20 mol %; (□) 30 mol %; (○) 40 mol %.

to be of the order of 10 Pa s between 55 and 65 °C for the precursor prepared from EOPA-TBZ (Al/Zr = 9/1)–30 mol % AcOH.

The increase of viscosity corresponds to the increased amount of 5-coordinated aluminium in the precursor as shown in Fig. 2. However, the precursor comprising 6-coordinated aluminium shown in Fig. 2c was a solid, and showed no fluidity for spinning. 5-Coordinated aluminium is necessary for the appropriate fluidity in the present precursor. The increase of viscosity also originates from the increase in molecular weight as shown in Section 3.1.5.

3.3. Synthesis of alumina–zirconia powder from polymeric Al–Zr precursor

The precursor polymer was pyrolysed in air from room temperature to 500 °C yielding a greyish white solid in a yield of 25% by weight. Then, the product was heat treated at temperatures between 800 and 1300 °C for 1 h in air.

3.3.1. Crystallization process

The XRD profiles of the products are shown in Fig. 6, when the polymer was synthesized from EOPA-TBZ (Al/Zr = 9/1, 18.2 mol % ZrO_2) and 30 mol % AcOH. γ -Alumina of low crystallinity was formed at 800 °C as shown in Fig. 6a. The broad diffractions of tetragonal zirconia appeared after heat treatment at 1000 °C for 1 h (Fig. 6b). The crystallinity of zirconia increased on increasing the heat-treatment temperature from 1000 °C to 1200 °C as shown in Fig. 6b and c. γ -Alumina began to be transformed to α -alumina at 1200 °C, and was converted completely to α -alumina at 1300 °C.

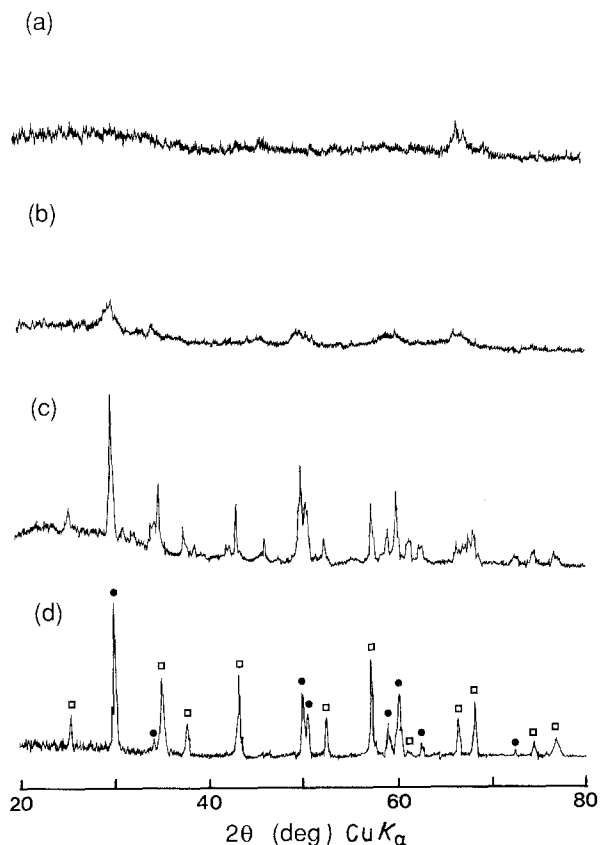


Figure 6 X-ray diffraction of the pyrolysed product of EOPA-TBZ (Al/Zr = 9/1) at temperatures from 800–1300 °C for 1 h. (a) 800 °C; (b) 1000 °C; (c) 1200 °C; (d) 1300 °C. (●) t-ZrO₂, (□) α-Al₂O₃.

3.3.2. Tetragonal phase in alumina-zirconia

The amount of tetragonal zirconia in the heat-treated product at 1300 °C for 1 h was estimated according to Garvie and Nicholson [12]. Only the tetragonal phase was observed for the precursor with the ratio of Al/Zr from 9/1 (18.2 mol % ZrO₂) to 7.5/2.5 (40.0 mol % ZrO₂). Tetragonal phase decreased in amount from 100% to 76% with the formation of monoclinic phase, on increasing the ratio of zirconium from Al/Zr = 7.5/2.5 to 7/3 (46.2 mol % ZrO₂) in the starting compound.

The product heat treated at various temperatures for 1 h was synthesized from EOPA-TBZ (Al/Zr = 9/1, 18.2 mol % ZrO₂) and contained zirconia particles of various sizes as shown in Fig. 7. The median diameter of zirconia particles increases from 9.0 nm to 33 nm as the heat treatment temperature is raised from 560 °C to 1300 °C. The size of the zirconia particles is below 80 nm after heat treatment at 1300 °C for 1 h.

3.4. Synthesis of alumina-zirconia fibre from Al-Zr precursor

The aluminium-zirconium precursor was extruded through a spinneret at temperatures from 55–65 °C, and then fired in air above 800 °C.

Alumina-18.2 mol % zirconia fibres synthesized from the polymer fibre at 1300 °C are shown in Fig. 8. The disruption-free fibre was synthesized from the precursor fibre. The diameter of fibre ranged from 20–100 μm. The cross-section of the fibre shown in

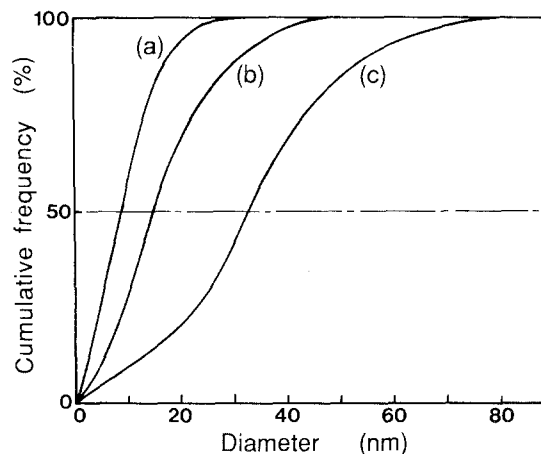


Figure 7 Size distribution of zirconia particles in alumina matrix formed from EOPA-TBZ (9/1)–30 mol % AcOH at various temperatures. (a) 560 °C, 1 h; (b) 1000 °C, 1 h; (c) 1300 °C, 1 h.

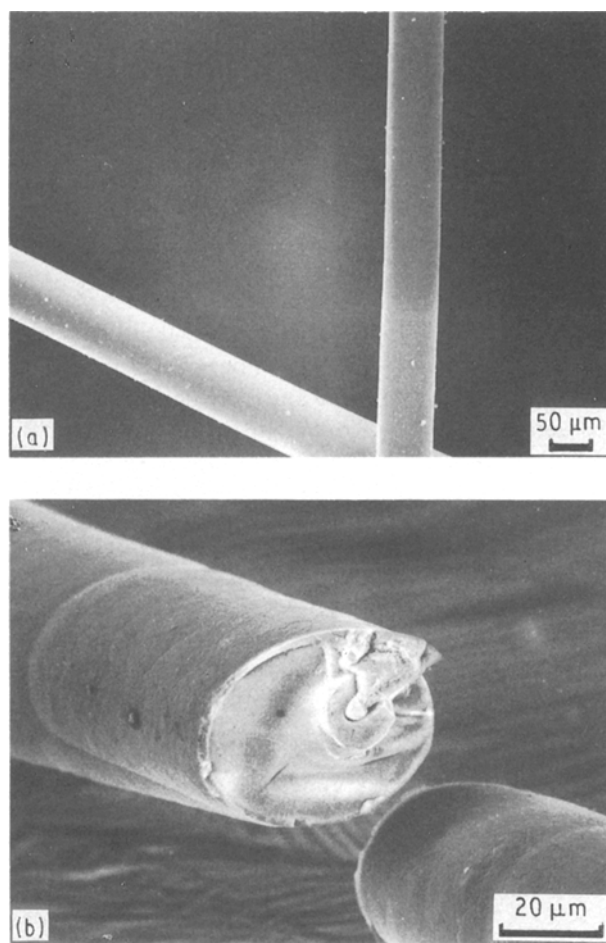


Figure 8 Scanning electron micrographs of alumina-zirconia fibres prepared from EOPA-TBZ (9/1)–30 mol % AcOH, after heat treatment at (a) 1300 °C for 1 h, (b) at 1300 °C for 6 h.

Fig. 8b is almost circular, and contains no pores. The fibre consists of quite small grains, and is practically fully dense.

Fig. 9 shows the Raman microprobe spectrum of the fibre (diameter 50 μm) prepared from EOPA-TBZ (9/1)–30 mol % AcOH at 1300 °C for 1 h. The scattering pattern shown in Fig. 9 had the characteristic bands of tetragonal zirconia at 142 and 269 cm⁻¹,

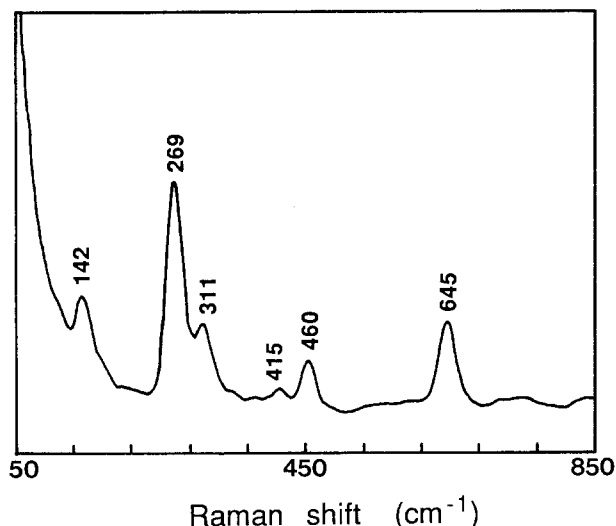


Figure 9 Raman microprobe spectrum of alumina-zirconia fibre synthesized from EOPA-TBZ (9/1) at 1300 °C.

and was in agreement with that reported [19, 20]. The doublet at 181 and 192 cm^{-1} due to monoclinic phase was not observed. The small band at 415 cm^{-1} is derived from α -alumina. Because alumina is known to show very weak Raman scattering, the scatterings of tetragonal zirconia were detected predominantly.

4. Conclusions

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

1. The precursor for alumina-zirconia was synthesized by the reaction of ethyl 3-oxobutanoate-diisopropoxyaluminium and zirconium tetrabutoxide in the presence of glacial acetic acid.

2. The precursor suitable for spinning had a molecular weight below 1000, and included an appropriate amount of 5-coordinated aluminium.

3. The viscosity of the polymer was controlled by the amount of acetic acid as well as the working temperature for spinning.

4. The particle size of tetragonal zirconia dispersed in α -alumina was below 80 nm after heat treatment of EOPA-TBZ (9/1) at 1300 °C for 1 h.

5. The preceramic fibre melt-spun from the polymer was converted to alumina-zirconia fibre with a uniform and fine grain size after heat treatment at 1300 °C.

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