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Synthesis of polycrystalline zirconia fibre with organozirconium precursor

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Polycrystalline zirconia fibre was successfully synthesized by pyrolysis of preceramic fibre formed from an organozirconium compound. Dibutoxybis(2, 4-pentadionato)zirconium (BPZ) was polymerized at 150° C and 10^2 Pa, yielding a viscous polymeric product. The infrared absorption bands of the Zr–O bond changed from separate to coalesced bands after polymerization. The signals of the ^{13}C NMR spectrum of BPZ changed from sharp singlets to multiplets after polymerization. The molecular weight of the polymer was between 400 and 1000. The viscosity of polymer was 580 Pa sec at 30° C and a shear rate of $1.0\,\mathrm{sec}^{-1}$. The polymer viscosity decreased with increased temperature from 30 to 60° C. The precursor polymer pyrolysed at 400° C in air was amorphous to X-rays, and crystallized in a mixture of monoclinic and tetragonal phases at 450° C. Tetragonal zirconia was synthesized from the polymer including 4.3 mol% yttrium compound (2.2 mol% yttria) after heat treatment at 1200° C for 1 h. The precursor fibres were pyrolysed to yield fine-grained fibres of tetragonal zirconia at 1200° C for 1 h.

1. Introduction

Ceramic fibres have growing applications for the reinforcement of metals, plastics and ceramics. Garvie *et al.* [1] reported the high strength of tetragonal zirconia, and the absorption of fracture energy by the tetragonal–monoclinic transformation. Fine-grained tetragonal zirconia fibre was demonstrated to have a high strength from 1.5 to 2.6 GPa [2].

The solution technique has been used for the synthesis of the ceramic fibre precursor, since refractory oxides have extremely high melting points as well as low viscosity of melts. Zirconia fibres have been fabricated using sol–gel processing. The precursor fibre was spun from a viscous sol prepared by the hydrolysis of zirconium compounds, such as zirconium acetate [2–5] or oxychloride [3, 4]. The aqueous solution containing zirconium compounds was condensed and/or polymerized until an appropriate viscosity for spinning was reached. Zirconium alkoxide was hydrolysed to synthesize polyzirconoxane, which was converted to zirconia fibre [6].

Usually, the viscosity of the sol is time-dependent, and changes very rapidly once the formation of cross-linkage starts. On the other hand, the advantage of a 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.

We describe the synthesis of zirconia fibres from an organozirconium compound. The precursor polymer was synthesized by the thermal polymerization of a zirconium chelate compound. The polymeric precursor was analysed by infrared (IR), ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The viscosity of the polymer was investigated using a rotational viscometer. Crack-free zirconia fibres of tetragonal allotrope were prepared from the polymer fibres, which were spun from the polymeric organozirconium compound.

2. Experimental procedures

2.1. Starting materials

Acetylacetone (2, 4-pentadione, acac) and zirconium tetrabutoxide ($\mathrm{Zr(O^nBu)_4}$) were commercially available. Yttrium triisopropoxide ($\mathrm{Y(O^iPr)_3}$) was prepared according to Mazdiyasni *et al.* [7].

2.2. Synthesis of zirconia

The following procedure for the synthesis of $\mathrm{ZrO_2}$–2.2 mol% $\mathrm{Y_2O_3}$ is representative. Acetylacetone (122 mmol) was added drop by drop to a solution of $\mathrm{Zr(O^nBu)_4}$ (58.2 mmol) and $\mathrm{Y(O^iPr)_3}$ (2.6 mmol) in 100 ml benzene at room temperature. The reaction mixture was refluxed for 2 h to give a pale yellow transparent solution. Benzene and isopropanol were evaporated from the solution *in vacuo*, yielding a yellow oil. The residue was heated from room temperature to 150° C at 10^2 Pa yielding a red-brown liquid. The resultant product was pyrolysed in air from room temperature to 400° C at $1^\circ\mathrm{C\,min^{-1}}$. The pyrolysis product was heat-treated at temperatures between 450 and 1200° C for 1 h.

The polymer fibre was spun from the bulk polymer using a glass rod. The polymer fibre dried at room temperature, and then fired from room temperature to 800° C at $0.2^\circ\mathrm{C\,min^{-1}}$ in air. The ceramic fibre was subsequently heat-treated at 1200° C for 1 h.

2.3. Characterization of products

The organic product was characterized using IR and

NMR spectra. IR spectra of polymers were measured by the liquid film method. ^1H and ^{13}C NMR spectra were measured in $CDCl_3$ solution using tetramethylsilane as an internal standard. 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 room temperature to 60° C.

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

3. Results and discussion

3.1. Synthesis and characterization of polymeric organozirconium compound

3.1.1. *Synthesis of polymeric organozirconium compound*

Acetylacetone (2,4-pentadione) was reacted with zirconium tetrabutoxide to give a white solid. The formation of dibutoxybis (2,4-pentadionato) zirconium (BPZ) was confirmed by IR, ^1H and ^{13}C NMR spectroscopy. BPZ was heat-treated from room temperature to 150° C under vacuum to yield a red-brown liquid. The product was a liquid with extremely high viscosity at room temperature, and was soluble in organic solvents, such as benzene and chloroform.

Dibutoxybis (2,4-pentadionato) zirconium was found to be thermally more unstable than diisopropoxybis (2,4-pentadionato)zirconium (PPZ), which was distilled at 129° C and 67 Pa without polymerization [8].

3.1.2. *IR spectroscopy*

The IR spectra of starting BPZ and polymer are shown in Fig. 1. The absorption bands of the Zr–O bond, from 400 to 540 cm^{-1} [9, 10] in the starting BPZ, changed from separate to coalesced bands after polymerization. This change suggests the formation of the product with various kinds of Zr–O bonds from the starting single compound. The absorption bands ascribed to acetylacetonato ligands at 1570, 1520 and 1300 cm^{-1} [10] were observed in both compounds.

3.1.3. *^{13}C NMR spectroscopy*

The ^{13}C NMR spectra shown in Fig. 2 reveal the marked differences between BPZ and the polymer. The signals of BPZ in Fig. 2a were assigned as follows: $\delta = 14.0$ p.p.m. ($\underline{C}H_3CH_2CH_2CH_2O$), 19.0 p.p.m. ($CH_3$-$\underline{C}H_2CH_2CH_2O$), 35.5 p.p.m. ($CH_3CH_2\underline{C}H_2O$), 64 to 72 p.p.m. ($CH_3CH_2CH_2\underline{C}H_2O$), 26.9 p.p.m. ($\underline{C}H_3$-$COCHCO\underline{C}H_3$). 190.3 p.p.m. ($CH_3\underline{C}OCH\underline{C}OCH_3$), 103.2 p.p.m. ($CH_3CO\underline{C}HCOCH_3$). The number at the top of the signal in Fig. 2 corresponds to the number on each carbon of the molecular structure. The assignment of signals is in accord with Breitmaier and Voelter [11]. The integration of the signal shows that the C-4 carbon of the butoxy group diffuses from 64 to 72 p.p.m., because of the fast exchange of the OBu group on zirconium in the $CDCl_3$ solution.

The single signal corresponding to each carbon of

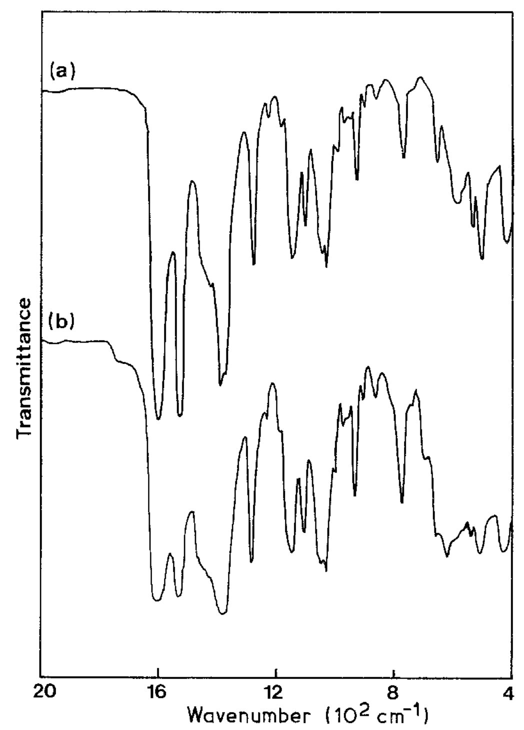

Figure 1 Infrared spectra of starting zirconium compound and polymer. (a) Dibutoxybis (2, 4-pentadionato) zirconium (BPZ); (b) polymeric product formed at 150° C and 10^2 Pa.

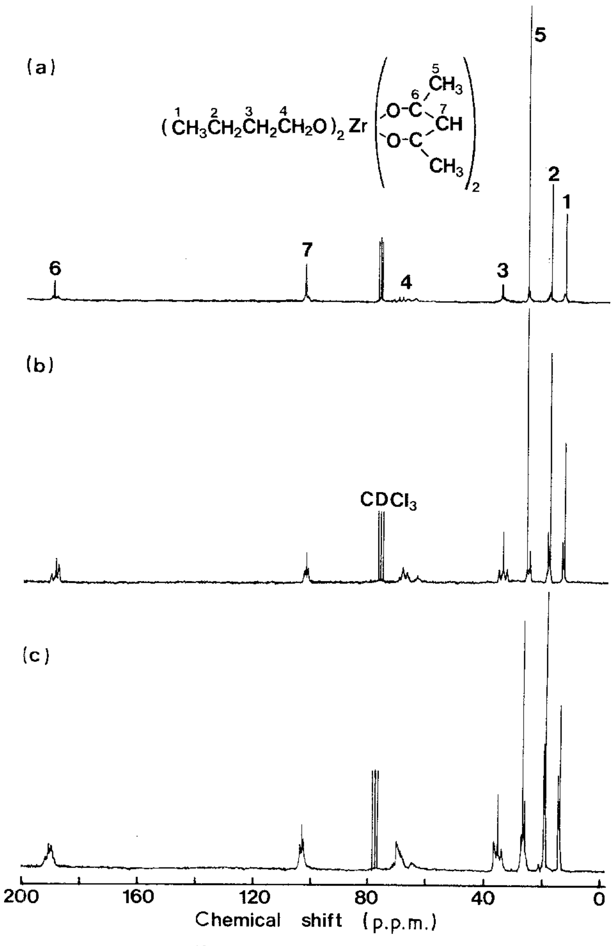

Figure 2 Change of ^{13}C NMR spectra of BPZ with temperature from 25 to 150° C under 10^2 Pa. (a) 25° C at 10^2 Pa; (b) 80° C at 10^2 Pa; (c) 150° C at 10^2 Pa.

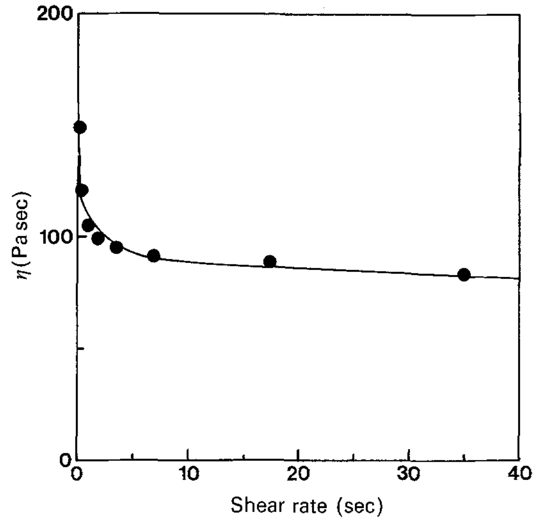

Figure 3 Change of viscosity (η) of polymer with shear rate at 40° C.

BPZ was changed to several signals with increased temperature from 80 (Fig. 2b) to 150° C (Fig. 2c). The triplets of C-6 and C-7 carbon indicate that at least three kinds of acetylacetonato ligands are formed in a mixture at 80° C (Fig. 2b). The result suggests that the reaction starts at about 80° C. The multiplets of each signal in Fig. 2c result from various kinds of carbons having a slightly different chemical environment from each other.

The presence of the butoxy group in the polymeric product shows that the heating redistributes the organic ligands on zirconium, yielding a mixture of various kinds of chelate compounds, such as $(BuO)_{4-n}Zr(acac)_n (n < 4)$. Also, the organic ligands of BPZ seem to undergo cross-linkage during heating, giving the polymeric product.

3.1.4. Molecular weight

The molecular weight of BPZ was 400 ± 30 (calculated for BPZ, 435.7) with cryoscopic measurements in benzene. Therefore the starting BPZ is monomeric in benzene. On the other hand, the polymeric product had a molecular weight of 810 ± 40 according to the cryoscopic measurement.

The polymer structure was analysed by mass spectrometry. The FAB MS spectrum of the polymer contained the fragmentation peaks of a mass unit of 306, which corresponded to a $Zr(acac)_2$-O unit. The fragment at 988 was attributed to $BuO-(Zr(acac)_2-O)_3$. The FD MS spectrum revealed that the precursor polymer had a distribution of (mass/electric charge) m/e peaks from 400 to 1000.

3.1.5. Structure of polymeric product

The polymeric product has 2,4-pentadionato (acac) and butoxy ligands on the basis of IR and ^{13}C NMR spectroscopy. The oligomer in the polymeric product has a structure unit of $(Zr(acac)_2-O)_3$. A mixture of $(BuO)_{4-n}Zr(acac)_n (n < 4)$ appears to constitute low molecular weight components of less than 500. The polymeric product consists mainly of monomeric chelate compounds and their oligomers.

3.2. Viscosity and spinnability of polymer

The changes of viscosity (η) of the polymer with shear rate at 40° C are shown in Fig. 3. Since the viscosity of polymer decreased with shear rate, the polymer is non-Newtonian. The distribution of molecular weight is responsible for the non-Newtonian behaviour of the polymer.

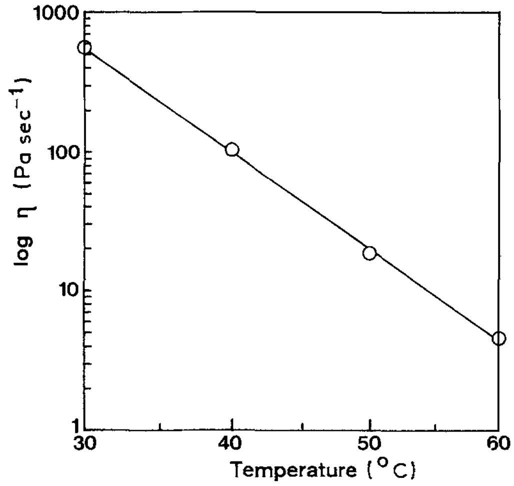

Figure 4 Variation of viscosity (η) with measurement temperature from 30 to 60° C at a shear rate of 3.5 sec^{-1}

The variation of viscosity (η) with measurement temperature at a shear rate of 3.5 sec^{-1} is shown in Fig. 4. The viscosity of the polymer was extremely high at room temperature, and decreased in magnitude from 5.63×10^2 Pa sec to 4.45 Pa sec with increasing temperature from 30 to 60° C.

The length of the polymer fibre with hand-spinning was > 50 cm at 30° C, and decreased with increasing spinning temperature from 30 to 60° C.

The room-temperature viscosity above 10^3 Pa sec was too high for the fabrication of fibres by hand-spinning. The viscosity of the present polymer suitable for hand spinning was found to be of the order of 10^2 Pa sec between 30 and 40° C.

3.3. Synthesis of zirconia from organozirconium precursor

The precursor polymer was pyrolysed in air from room temperature to 400° C, yielding a greyish-white solid in a yield of 36% in weight. The product was then heat-treated at temperatures between 450 and 1200° C for 1 h in air.

The XRD profiles of the products are shown in Fig. 5, when the polymer was synthesized from a mixture of BPZ and 4.3 mol % yttrium triisopropoxide (2.2 mol % yttria). The product at 400° C was amorphous to X-rays (Fig. 5a), and crystallized in tetragonal zirconia after heat treatment at 450° C for 1 h (Fig. 5b). The crystallinity of zirconia increased with increasing heat-treatment temperature from 800 to 1200° C, as shown in Figs 5c and d.

The amorphous product formed from the polymer without any yttrium compound at 400° C began to crystallize in tetragonal and monoclinic phase at 450° C.

3.4. Conversion of polymer fibre to ceramic fibre

Polymer fibres were spun from the organozirconium precursor at 35° C, and then fired in air above 800° C.

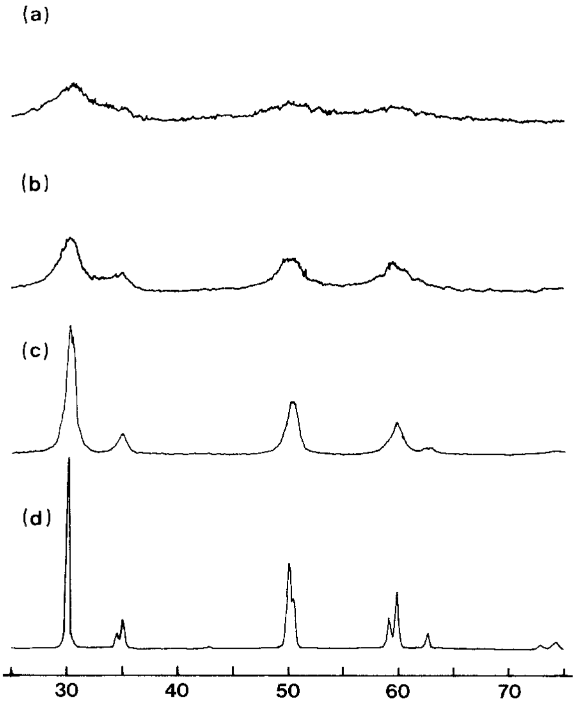

Figure 5 X-ray diffraction profile of ZrO_2–2.2 mol % Y_2O_3 after heat treatment between 400 and 1200° C. (a) 400° C for 1 h; (b) 450° C for 1 h; (c) 800° C for 1 h; (d) 1200° C for 1 h.

The zirconia fibre without any yttria has cracks due to phase transformation, as shown in Fig. 6a. The fibre was very fragile to handle.

Zirconia–2.2 mol % yttria fibres synthesized from the polymer fibre at 800 and 1200° C are shown in Figs 6b and c, respectively. The disruption-free fibre was synthesized from the organozirconium fibre. The fibre diameter ranged from 3 to 100 μm. The fibres were more flexible than that shown in Fig. 6a. The grain size of the fibre was less than 0.3 μm. No pores are observed in the fracture surface, as shown in Fig. 6c.

The thick fibre of diameter ~ 100 μm was confirmed to be tetragonal zirconia by XRD analysis.

4. Conclusions

Tetragonal zirconia fibre was synthesized successfully from organozirconium precursor without any additives of polymer for the adjustment of viscosity.

The results are summarized as follows:

1. The thermal polymerization was utilized for the synthesis of polymer from dibutoxybis (2, 4-pentadionato)zirconium.
2. The polymeric product was a mixture of chelate compounds and oligomers, and had a molecular weight below 1000.
3. The viscosity of the bulk polymer was dependent on shear rate, and was controlled by the selection of temperature in order to obtain the appropriate viscosity for spinning.
4. The preceramic fibre spun from the polymer was converted to tetragonal zirconia fibre with uniform and fine grain size after heat treatment at 1200° C.

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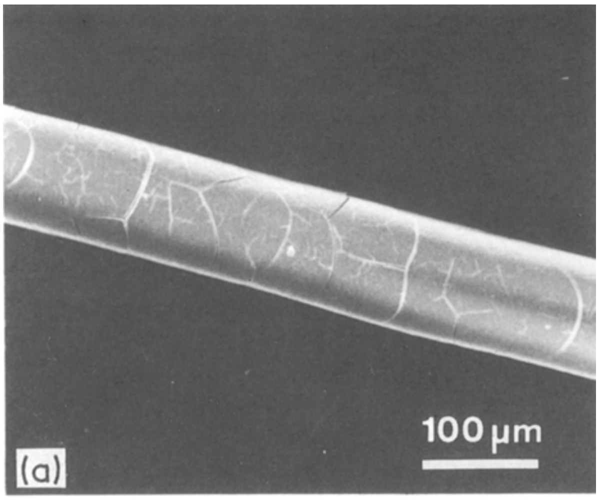

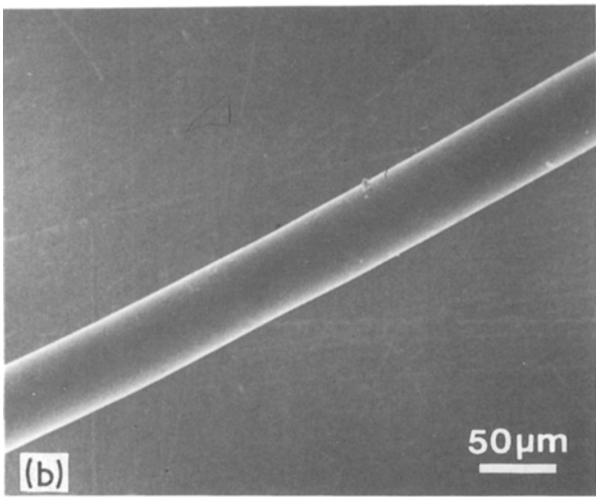

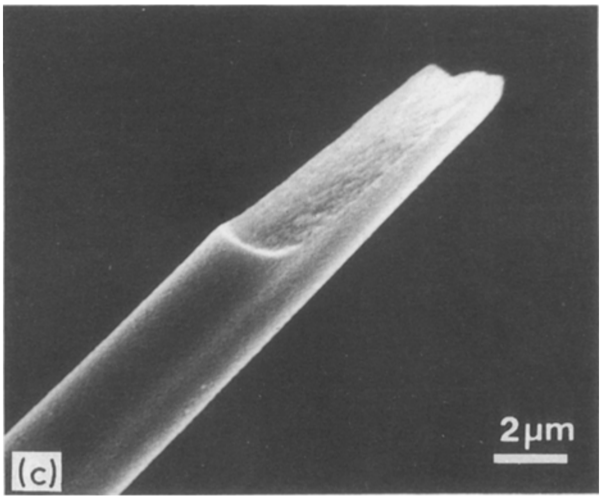

Figure 6 SEM pictures of zirconia fibres. (a) No yttria at 800° C for 1 h; (b) 2.2 mol % yttria at 800° C for 1 h; (c) 2.2 mol % yttria at 1200° C for 1 h.

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