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Production mechanism of polyzirconocarbosilane using zirconium(IV)acetylacetonate and its conversion of the polymer into inorganic materials

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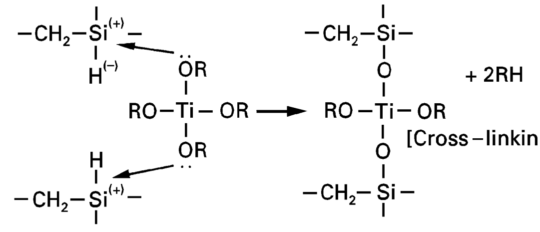
The reaction of polycarbosilane with zirconium(IV)acetylacetonate proceeded at 573 K in nitrogen atmosphere by the condensation reaction of the Si–H bonds in polycarbosilane and the ligands of zirconium(IV)acetylacetonate accompanied by the evolution of acetylacetone, and then the molecular weight increased by the cross-linking reaction with a formation of Si–Zr bond. The obtained polyzirconocarbosilane showed higher ceramic yield than the polycarbosilane. Zirconium contained in the pyrolysed polyzirconocarbosilane was furthermore found to have the effect of inhibiting crystalline grain growth of β-type SiC up to high temperature, so Si–Zr–C–O fibre, which was obtained by the use of polyzirconocarbosilane as precursor, showed high tensile strength up to high temperature.

1. Introduction

Many investigations on preceramic polymers, which have high ceramic yield, have been actively performed [1–5]. Of these, silicon containing polymers have been most vigorously developed. Polymers of this kind have almost been prepared by condensation of chlorosilanes using active metal, transition metal catalysed ring-opening polymerization or condensation of chlorosilane with amine (or NH_3). Linear polymers, however, are not useful ceramic precursors, because their pyrolysis over 1273 K under a stream of inert gas result in little or no ceramic residue [6–8]. In order to obtain higher ceramic yield, preceramic polymer should have cross-linked structure, ring structure and/or cross-linkable structure during the initial stages of the pyrolysis [9]. Many approaches with this objective in mind have been developed [2, 9, 10].

Polycarbosilane, which is obtained by thermal rearrangement reaction of polydimethylsilane, has high ceramic yield, and so the polycarbosilane is available for preceramic polymer [11]. The polycarbosilane has some cross-linking points and ring structures, which are composed of Si–Si bonds or Si–CH_2–Si bonds, and then the cross-linking reaction proceeds during the initial stages of the pyrolysis [12, 13]. Polytitanocarbosilane, which is produced by condensation reaction of the polycarbosilane with titanium(IV)tetra-alkoxide, has much higher ceramic yield than the polycarbosilane because the polytitanocarbosilane has several cross-linking points composed of Si–O–Ti–O–Si bonds as given below [14]



Moreover, it has been known that the titanium, which is contained in the cross-linking point of the polytitanocarbosilane, plays an important role in the enhancement of the Si–C bonding energy of the pyrolyzed polytitanocarbosilane, and the inhibition of crystalline grain growth of β-SiC up to high temperature [14].

A preceramic polymer, which is synthesized by the use of organic zirconium compounds instead of organic titanium compounds, similarly shows high ceramic yield [15]. However, the production mechanism, the polymer's structure and the pyrolysis properties of this zirconium containing polymer has not been clarified in detail.

In this work, the detailed production mechanism of the polyzirconocarbosilane by the reaction of polycarbosilane with zirconium(IV)acetylacetonate was clarified, and the pyrolysis properties of the inorganic fibre, which was obtained by the use of the

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polyzirconocarbosilane, were also investigated. These results are reported here.

2. Experimental procedure

2.1. Synthesis of polycarbosilane and polyzirconocarbosilane

Polyzirconocarbosilane (PZC) was prepared by the reaction of polycarbosilane (PCB) with zirconium(IV) acetylacetonate (5.87×10^{-4} mol/PCB1g) at 573 K in a stream of nitrogen gas. The PCB was synthesized by the reaction of polydimethylsilane (100 g) [16], with polyborodiphenylsiloxane (3 g) [17] at 613 K under nitrogen atmosphere for 8 h. The weight average molecular weight, $\bar{M}_w$, of PCB was 1000.

2.2. Measurements

Gel-permeation chromatograms (GPC) were taken with a Toyo Soda HCL-801 A, with G-400 HXL, G-3000 HXL, G-2000 HXL (× 2) and G-2000 H8 (× 2) packing and tetrahydrofuran cluent at a flow rate of $1\,\mathrm{ml\,min^{-1}}$ at 313 K using polystyrene as a standard specimen.

Infrared spectra were measured in a $2\,\mathrm{g\,l^{-1}}$ *n*-hexane solution with a Hitachi IR-430 grating infrared spectrometer with a 0.1 cm light-path length of the solution cell. The absorptivities of Si–H, $Si–CH_2–Si$ and $Si–CH_3$ bonds in starting material and polymerized products were calculated from the following equation

$$K = \frac{1}{CL}\log(I_0/I)$$

where K is the absorptivity ($\mathrm{g^{-1}\,cm^{-1}}$), C the concentration ($\mathrm{g^{-1}}$), L the light-path length (cm), $\log(I_0/I)$ the absorbance.

Gaseous by-products produced during the formation of PZC were separated from nitrogen gas at 200 K using dry ice/methyl alcohol and identified by means of gas chromatography and mass spectrometry. The quantity of the by-product was directly determined by gravimetric technique.

Thermogravimetric analysis (TGA) was carried out using a Rigaku Micro TG-DTA (high-temperature type) machine by raising the temperature at $5\,\mathrm{K\,min^{-1}}$ up to 1673 K in a N_2 flow of $50\,\mathrm{cm^3\,min^{-1}}$.

Chemical analysis of PZC and pyrolysed PZC was made for five elements: Si (by a gravimetric method); Zr (by a calorimetric method); C (by a combustion volumetric method); O (by gas analysis); and H (by gas analysis).

The pyrolysed PZC was pulverized, and X-ray diffraction pattern of this powder was recorded with a Rigaku X-ray diffractometer using CuK_α radiation with a nickel filter.

The tensile strength of Si–Zr–C–O fibre, which was obtained by the use of PZC, was measured using a universal testing machine (Tosoku Measuring Co Ltd., Tensilon CFT-200) (150 mm gauge length and $60\,\mathrm{mm\,min^{-1}}$ cross-head speed at room temperature). The diameters of the fibre were determined using a Sena dynascope, Model 4DM.

3. Results and discussion

3.1. The reaction process of polycarbosilane with zirconium(IV)acetylacetonate

Fig. 1 shows the GPC curves of PCB and PZC. The broad peak in the high molecular weight region of PZC's GPC curve is found to be higher than that of PCB. The change in the weight average molecular weight, $\bar{M}_w$, of the product during the reaction of PCB with zirconium(IV)acetylacetonate is shown in Fig. 2. As seen from this figure, the $\bar{M}_w$ increases with reaction time and the extent of the increase in $\bar{M}_w$ becomes smaller as the reaction of PCB with zirconium (IV) acetylacetonate proceeds.

The infrared spectra of PCB, PZC and zirconium(IV)acetylacetonate, are shown in Fig. 3. In the case of PCB and PZC, the absorptions at $2950\,\mathrm{cm^{-1}}$ (C–H stretching), $2100\,\mathrm{cm^{-1}}$ (Si–H stretching), $1400\,\mathrm{cm^{-1}}$ (C–H deformation), $1350\,\mathrm{cm^{-1}}$ (CH_2 deformation of $Si–CH_2–Si$–bond), $1250\,\mathrm{cm^{-1}}$ (Si–Me

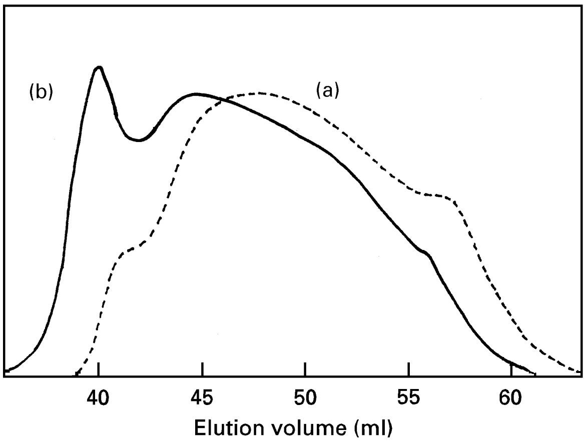


Figure 1 GPC of (a) PCB and (b) PZC.

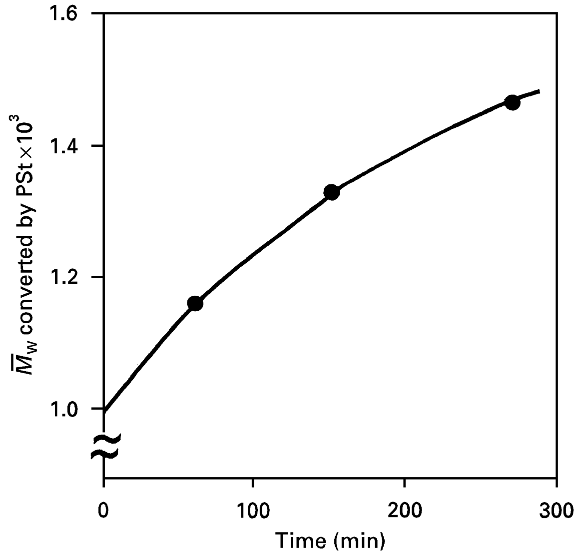


Figure 2 M_w of the product obtained by the reaction of PCB with zirconium(IV)acetylacetonate as a function of the reaction time.

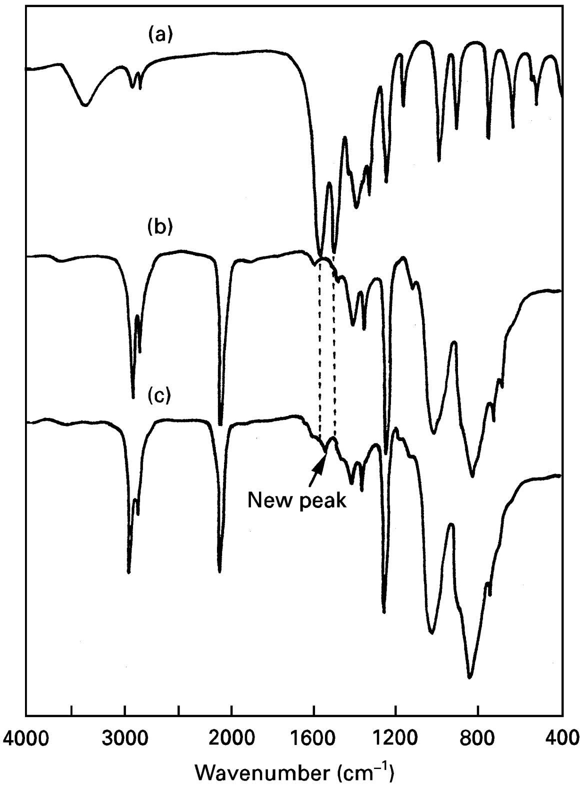


Figure 3 IR spectra of (a) zirconium(IV)acetylacetonate, (b) PCB, and (c) PZC.

deformation), 1040 cm^{-1} (Si–O stretching), 1020 cm^{-1} (CH_2 wagging of Si–CH_2–Si bond), 820 cm^{-1} (Si–C stretching) are observed. On the other hand, in the case of zirconium(IV)acetylacetonate, the characteristic adsorptions at 1580 cm^{-1} (C = O stretching) and 1515 cm^{-1} (C = C stretching) are observed. In the absorption of PZC, which was synthesized by the reaction of PCB and zirconium(IV) acetylacetonate, an enormous decrease in the number of Si–H bond is recognized. Further, in the absorption of PZC, appearance of a new peak at 1540 cm^{-1}, which is not present in either absorptions of PCB or zirconium(IV)acetylacetonate, is recognized. It is assumed that the reaction of PCB with zirconium(IV)acetylacetonate results in the delocalization of the electron of C = O bond in zirconium(IV)acetylacetonate and/or the localization of the electron of C = C bond in zirconium(IV)acetylacetonate.

Fig. 4 shows the changes in infrared absorptivities at 2100, 1400, 1350 cm^{-1} corresponding to Si–H bond, Si–CH_3 bond and Si–CH_2–Si bond in PCB, respectively, during the reaction of PCB with zirconium(IV)acetylacetonate. As described above, an enormous decrease in the number of Si–H bonds is observed at the beginning of the reaction, whereas no changes in the numbers of Si–CH_3 and Si–CH_2–Si bonds are recognised.

The reaction of PCB with zirconium(IV)acetylacetonate was done in xylene solution under N_2 atmosphere. The result of gas chromatography analysis of the by-product, which was contained in xylene evolved from the reaction system, is shown in Fig. 5. In the gas chromatogram, three peaks (1, 2 and 3), which were identified as benzene, xylene and acetylacetone, respectively, by mass spectrometry, are recognized. Of these, the xylene, with a small amount of benzene, is the solvent of the reaction. It is considered that the acetylacetone is a by-product based on the ligand of zirconium(IV)acetylacetonate.

Fig. 6 shows the relationship between the quantity of acetylacetone as by-product and the reaction time. During the reaction of PCB with zirconium(IV) acetylacetonate (5.87 x 10^{-4} mol/PCB1g) at 573 K for 4.5 h, the quantity of evolved acetylacetone were 1.3 mmol/PCB1g. Accordingly, about half of ligands of zirconium(IV)acetylacetonate is found to be eliminated by the reaction. The chemical analysis of the obtained PZC is shown in Table I. As can be seen from these results concerning contents of Zr and O, it is considered that about half of ligands of zirconium(IV)acetylacetonate remains in the PZC after the reaction.

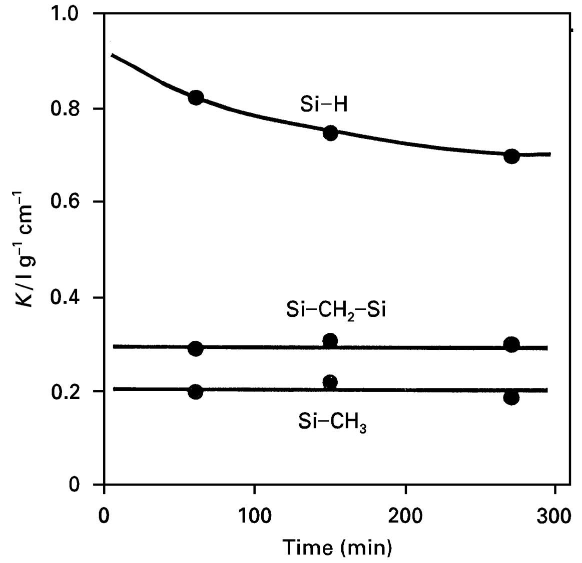


Figure 4 Changes in Si–H and Si–CH_2–Si bonds of the products during the reaction of PCB with zirconium(IV)acetylacetonate (5.87 x 10^{-4} mol/PCB1g) at 573 K.

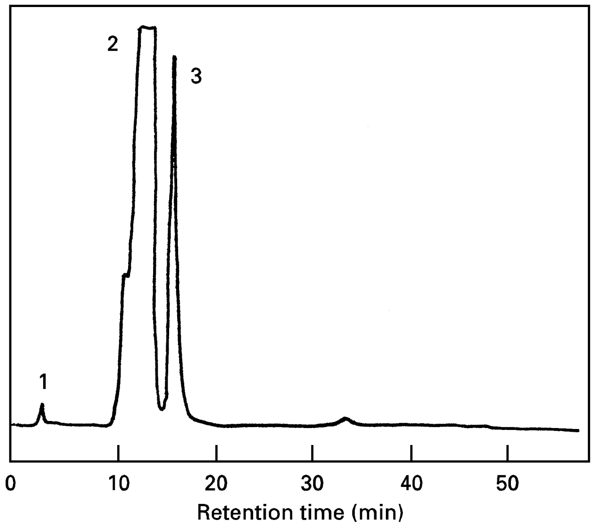
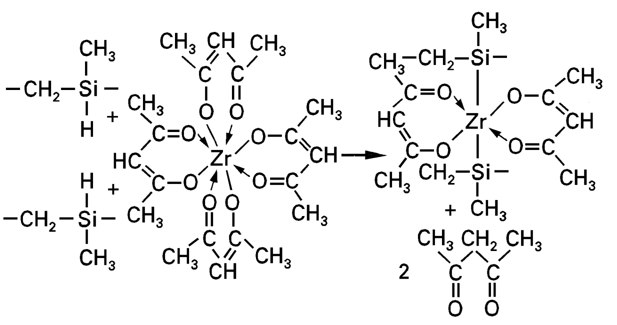


Figure 5 GC analysis of the by-product obtained by the reaction of PCB with zirconium(IV)acetylacetonate at 573 K.

From the aforesaid increase in the molecular weight with the decrease in the number of Si–H bonds and the evolution of the acetylacetone, the following reaction scheme was considered



As can be seen from this reaction scheme, the increase in the molecular weight by the cross-linking reaction with a production of Zr–Si bonds was estimated. It can be considered that donation from the occupied d π-orbitals of zirconium to the empty *d*-orbitals of silicon may play a significant part in the Zr–Si bonding [18, 19]. Actually, many low molecular weight compounds with Zr–Si bond are already known [20–22]. Generally, these compounds show fair colour. PZC also shows fair reddish orange. However, by exposure to air, this colour faded away with an increase in oxygen content in PZC. It has been shown that early metal–silicon bonds are quite reactive toward oxygen [23], and so the importance of excluding air in preparations of early metal-silyls has been emphasised. From this information, it was estimated that the fading of PZC's colour in air was carried out by insertion of oxygen in the Zr–Si bonds.

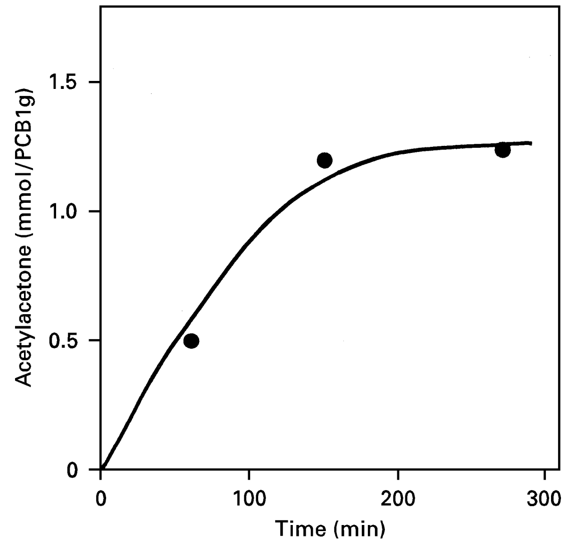


Figure 6 The relationship between the quantity of acetylacetone as by-product and reaction time.

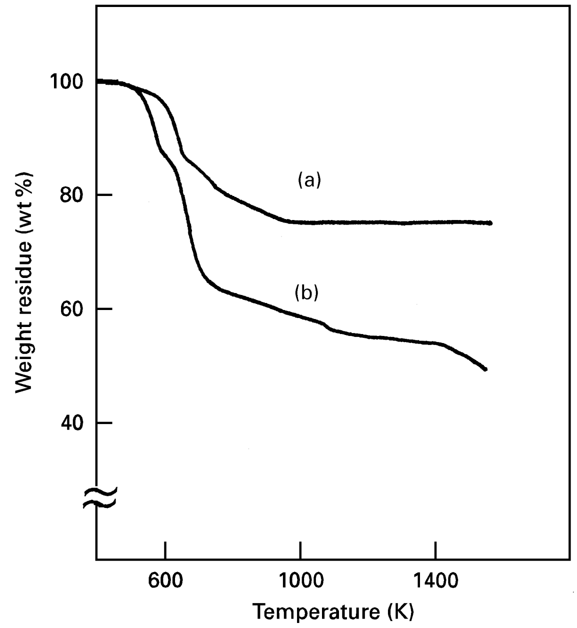


Figure 7 TG curves of (a) PZC and (b) PCB.

3.2. The conversion of PZC into inorganic material

Thermogravimetric (TG) analysis curves of the PZC and the PCB are shown in Fig. 7. TG analysis indicates that the organic groups of both polymers are decomposed below about 973 K, and then the weight residue of the PZC becomes larger than that of the PCB with increasing temperature up to 1573 K in a stream of nitrogen gas. The weight residues of the PZC and the PCB at 1573 K are 76 wt % and 51 wt %, respectively. Accordingly, the PZC is found to be better preceramic polymer with a higher ceramic yield than the PCB.

Fig. 8 shows X-ray diffraction patterns of pyrolysed PZC up to 1723 K in a stream of inert gas. X-ray diffraction patterns below 1623 K are very broad and indicate the amorphous state. The X-ray diffraction patterns above 1673 K show the crystallization of β-SiC. The crystalline sizes of β-SiC(1 1 1) at $2\theta = 35.6^\circ$ were estimated, using the Scherrer equation, to be 2.0, 3.6 and 6.0 nm at 1623, 1673 and 1723 K, respectively. In the same way, the crystallite sizes of β-SiC(1 1 1) of pyrolysed PCB were also estimated to be 3.3, 5.95 and 10.5 nm at 1623, 1673 and 1723 K, respectively. The crystalline grain size of pyrolysed PZC is found to be smaller than that of

TABLE I Chemical analysis of PZC and zirconium(IV)acetylacetonate

Compound	Chemical analysis (wt %)					Chemical formula	O/Zr (mole ratio)
	Si	C	O	H	Zr		
PZC[a]	43.82	38.98	3.30	9.12	4.78	$Si_1C_{2.08}H_{5.8}O_{0.13}Zr_{0.03}$	4.3
Zirconium (IV) acetylacetonate	–	49.26	26.25	5.79	18.71	$C_1H_{1.4}O_{0.4}Zr_{0.05}$	8.0

[a] Polymerization condition: zirconium(IV)acetylacetonate: 5.87×10^{-4} mol/PCB1g, 573 K; reaction time 4.5 h.

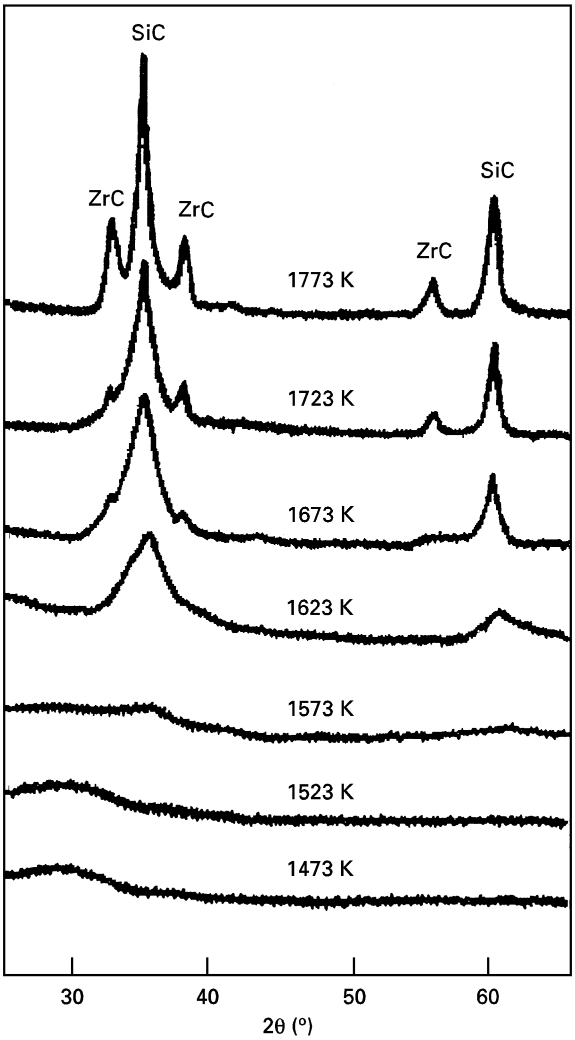


Figure 8 X-ray diffraction patterns of pyrolysed PZC up to 1723 K in a stream of inert gas.

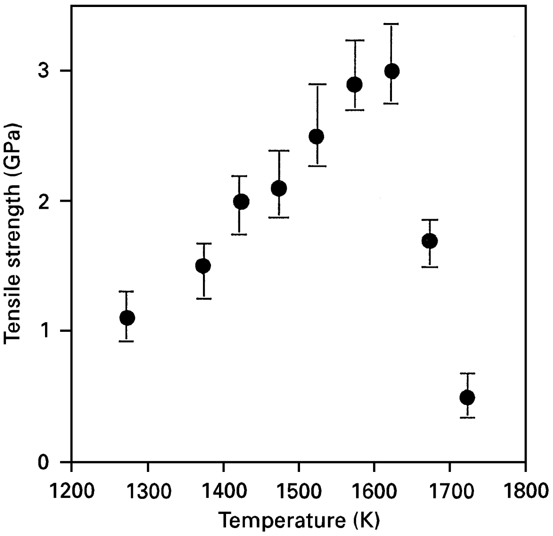


Figure 9 The tensile strength of the Si–Zr–C–O fibre prepared by the pyrolysing at various temperatures.

pyrolysed PCB. This phenomenon is similar to the phenomenon of pyrolysed polytitanocarbosilane which is synthesized from PCB with tetra-alkyltitanate [24, 25]. Consequently, zirconium contained in the pyrolysed PZC is also regarded as playing an important role in the inhibition of crystalline grain growth of β-SiC up to high temperature.

PZC can be continuously melt-spun and then cured in air by heating at 10–20 K min^{-1} to temperatures approaching 473 K. By pyrolysis of the curved PZC fibre at temperatures above 1273 K, Si–Zr–C–O fibre can be obtained. Fig. 9 shows the tensile strength of the Si–Zr–C–O fibre prepared by pyrolysing at various temperatures. The Si–Zr–C–O fibre has the maximum values at 1573 to 1623 K. The tensile strength of the Si–Zr–C–O fibre begins to decrease at a temperature above 1673 K. The decrease of the tensile strength is considered to be related to the crystallization of β-SiC, as can be seen in Fig. 8.

4. Conclusions

The reaction of PCB with zirconium(IV)acetylacetonate proceeded by the condensation reaction of the Si–H bonds in PCB and the ligands of zirconium(IV)acetylacetonate accompanied by the evolution of acetylacetone, to produce PZC. In this condensation reaction, the increase in the molecular weight by the cross-linking reaction with a formation of Zr–Si bonds was estimated. The weight residue of PZC was larger than that of PCB, so the PZC was found to be better preceramic polymer than the PCB. Zirconium contained in the pyrolysed PZC was considered to play an important role in the inhibition of crystalline grain growth of β-SiC up to high temperature. From these reasons, the Si–Zr–C–O fibre, which was produced by pyrolysing cured PZC fibre at high temperatures from 1573 K to 1623 K, showed excellent tensile strength reaching 3.0 GPa.

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