JOURNAL OF MATERIALS SCIENCE 23 (1988) 2589–2594

Development of a new continuous Si–Ti–C–O fibre using an organometallic polymer precursor

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A polytitanocarbosilane, which is useful as the precursor polymer for ceramic fibre, was synthesized using polydimethylsilane, polyborodiphenylsiloxane and titanium tetraisopropoxide. The polytitanocarbosilane was melt-spun and using the continuous heat-treatment process from the polymer fibre to ceramic fibre, flexible Si–Ti–C–O fibre was produced. The density, tensile strength and Young's modulus of this amorphous ceramic fibre were found to be 2.35 g cm^{-3}, 3.0 ± 0.2 and 220 ± 10 GPa, respectively. The Si–Ti–C–O fibre retained its high tensile strength to higher temperatures (about 1200° C). The specific resistance of this ceramic fibre covered a wide range of 10^7 to 10^{-1} Ω cm. This ceramic fibre is considered to be useful as reinforcement fibre for composites.

1. Introduction

The formation of ceramics such as silicon carbide or silicon nitride from various organosilicon polymers has been actively studied in recent years [1, 2]. The main advantage of the conversion from polymers to ceramics is that it is possible to prepare easily ceramic fibrous shapes which are difficult to synthesize by traditional inorganic chemical processes. On the basis of this advantage, both SiC fibre [3] and Si–N–O fibre [4] have been synthesized from polycarbosilane and then $Si_xN_yC_z$ fibre [5] and Si–N–C fibre [6] have been synthesized from polycarbosilazane and hydridopolysilazane, respectively. SiC fibre has been manufactured on an industrial scale with a trade name of Nicalon® by Nippon Carbon Co., Tokyo, Japan. This fibre has a high tensile strength and a high Young's modulus, and is very flexible, thus it is possible to fabricate two- and three-dimensional woven fabrics of this fibre. SiC fibre- or fabric-reinforced glass have been prepared [7] and infiltration of these fabrics with silicon carbide by the chemical vapour infiltration (CVI) method [8, 9] has been studied and the ceramic composites have been planned for use as high-temperature structural materials [10]. However, SiC fibre has a weak point: the mechanical properties deteriorate at higher temperature [3, 11].

Through further investigations of organosilicon polymers, a novel polytitanocarbosilane has been prepared which can be converted by pyrolysis into a mixture of silicon carbide and titanium carbide with a high yield. This polytitanocarbosilane is formed by the cross-linking of polycarbosilane with titanium compounds [12]. On the basis of the conversion process from polititanocarbosilane to ceramics, in this study we have prepared a polytitanocarbosilane which is easily spun and very useful as a precursor of ceramic fibres. Using this polymer, a new Si–Ti–C–O fibre with high tensile strength and Young's modulus has been synthesized by the continuous heat-treatment process from the melt-spun polytitanocarbosilane fibre. The method of synthesis and the mechanical properties of the Si–Ti–C–O fibre, and the pyrolysis process of the polytitanocarbosilane fibre are presented in this paper.

2. Experimental procedure

2.1. Synthesis of polytitanocarbosilane and Si–Ti–C–O fibre

Polytitanocarbosilane was synthesized by mixing polydimethylsilane (100 kg) [13] and polyborodiphenylsiloxane (3 kg) [14] with titanium tetraisopropoxide (10 kg). They were heated at 340° C under nitrogen gas for 12 h and then polytitanocarbosilane (PTC) was obtained. The polymer was concentrated at 320° C for 2 h in a stream of nitrogen gas and then PTC (70 kg) with a number average molecular weight ($\bar{M}_n = 1600$) was prepared. For reference, polycarbosilane (PC-B) [15] with $\bar{M}_n = 1400$ was prepared under the same conditions as PTC without the addition of the titanium tetraisopropoxide.

Si–Ti–C–O fibre was continuously prepared by melt-spinning PTC and PC-B at about 270° C using a multiple-hole nozzle and then PTC fibre and PC-B fibre were continuously wound on the drum placed below the nozzle. The drawing speed was about 500 m min^{-1}. This PTC polymer was easily spun in comparison with PC-B. After the spun PTC fibre and PC-B fibre were cured in air at 170 and 110° C,

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respectively, at a heating rate of 15° C h^{-1}, the cured PTC fibre and cured PC-B fibre were heat-treated continuously in the temperature range 800 to 1500° C in a stream of nitrogen gas to obtain continuous Si-Ti-C-O fibre and SiC fibre.

2.2. Measurements

Infrared spectra were measured using an Hitachi 285 grating infrared spectrometer by the KBr pellet method.

The number average molecular weights, $\bar{M}_n$, were measured using an Hitachi 115 molecular measurement apparatus by vapour pressure osmometry (VPO) in benzene solution, using benzil as the standard material.

Thermal gravimetric (TG) analysis was carried out using Rigaku Micro TG-DTA (high-temperature) machine by raising the temperature at 5° C min^{-1} up to 1400° C in a nitrogen flow of 50 cm^3 min^{-1}.

Si-Ti-C-O fibre and SiC fibre were pulverized, and X-ray diffraction patterns of their powders were recorded with a Rigaku X-ray diffractometer using Cu$K\alpha$ radiation with a nickel-filter.

The mechanical properties, tensile strength and Young's modulus, of the Si-Ti-C-O fibre and SiC fibre were measured using a universal testing machine (Tousoko Measuring Co Ltd) Tensilon CFT-200 (150 mm gauge length and 60 mm min^{-1} cross-head speed at room temperature). The diameters of the fibre were determined using the microscope with a Sena dynascope, Model 4DM.

Chemical analysis of PTC, PC-B, the Si-Ti-C-O fibre and SiC fibre was performed for seven elements: silicon (by a gravimetric method), titanium (by a colorimetric method), carbon (by a combustion volumetric method), boron (by an ICP method), and oxygen, hydrogen and nitrogen (by gas analysis).

3. Results and discussion

During heating the mixture of polydimethylsilane, polyborodiphenylsiloxane and titanium tetraisopropoxide, it is considered that cleavage of Si-Si bond in polydimethylsilane, the formation of Si-H and Si-CH_2-Si bonds, condensation of Si-H bonds and cross-linking by titanium compounds occur consecutively or simultaneously, and thus the main skeletons of PTC shown in Fig. 1 are considered to be formed. Polyborodiphenylsiloxane is considered to serve as the catalyst for the above reactions, similar to the case of PC-B [15, 16].

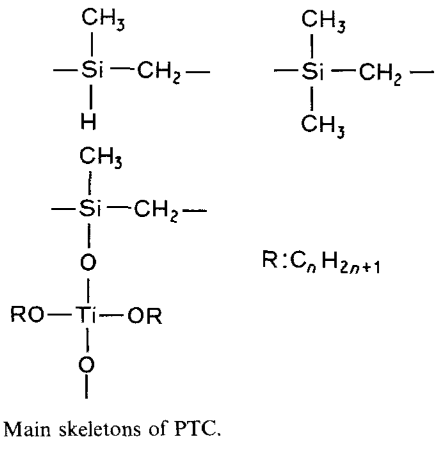

Figure 1 Main skeletons of PTC.

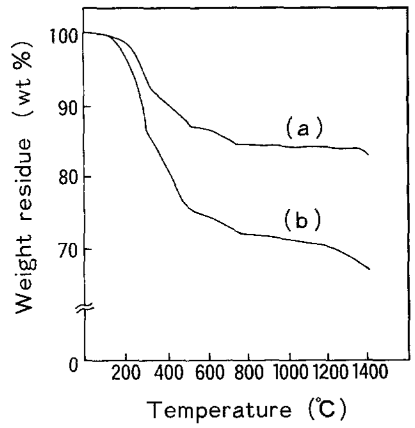

Figure 2 TG curves of (a) PTC and (b) PC-B.

Thermogravimetric (TG) analysis curves of the cured PTC fibre and the cured PC-B fibre are shown in Fig. 2. TG analysis indicates that the organic groups of both cured fibres are decomposed below about 700° C, and then the weight residue of the cured PTC fibre becomes larger than that of the cured PC-B fibre with increasing temperature up to 1400° C in a stream of nitrogen gas. Accordingly, PTC can be converted into Si-Ti-C-O compound with a high yield at a temperature above 800° C in nitrogen gas in comparison with the conversion of PC-B to SiC. For example, the weight residue of the cured PTC fibre and the cured PC-B fibre at 1400° C are 83 and 63 wt %, respectively.

The infrared spectra of the PTC fibre, the cured PTC fibre and the Si-Ti-C-O fibre obtained by the heat treatment of the cured PTC fibre at various temperatures in nitrogen gas are shown in Fig. 3. The absorption intensity at 2100 cm^{-1} (Si-H stretching) in the PTC fibre cured by oxidation, decreases and

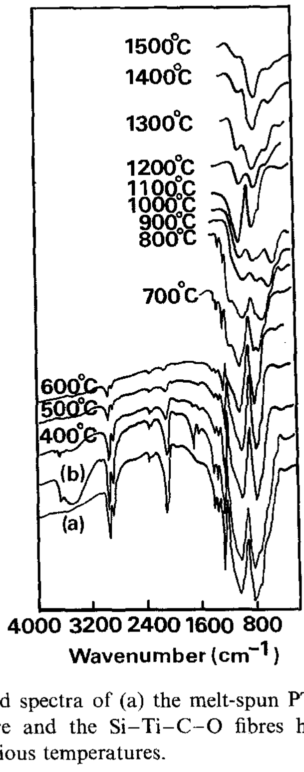

Figure 3 Infrared spectra of (a) the melt-spun PTC fibre, (b) the cured PTC fibre and the Si-Ti-C-O fibres heat-treated continuously at various temperatures.

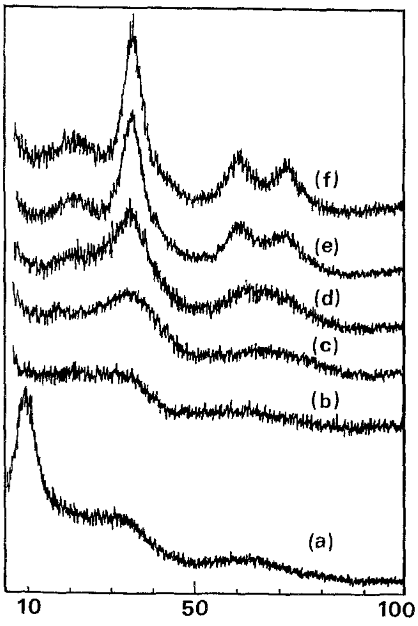

Figure 4 X-ray diffraction patterns of the cured PTC fibre and the Si–Ti–C–O fibres heat treated continuously at various temperatures: (a) cured PTC fibre, (b) heat treated at 800° C, (c) heat treated at 1100° C, (d) heat treated at 1300° C, (e) heat treated at 1400° C, (f) heat treated at 1500° C.

the intensity at about 1080 cm^{-1} (Si–O stretching) increases. It is considered that the curing mechanism of the PTC fibre is cross-linking of PTC molecules by oxidation, as in the case of the oxidation curing mechanism of polycarbosilane [17]. The conversion of the cured PTC fibre into the inorganic compound is brought to completion above about 700° C. This result is in good agreement with that observed in TG analysis. The absorption intensity at about 1080 cm^{-1} in Si–Ti–C–O fibre obtained at temperatures from 700 to 1300° C begins to decrease abruptly at 1400° C. This suggests that oxides with Si–O bonds react with free carbon and evolved CO gas in similar manner to that in the high-temperature pyrolysis process (above 1300° C) of polycarbosilane [11].

Fig. 4 shows X-ray diffraction patterns of the cured PTC fibre and Si–Ti–C–O fibres obtained by the heat treatment of the cured PTC fibre from 1100 to 1500° C in a stream of nitrogen gas. X-ray diffraction patterns below 1300° C are very broad and indicate the amorphous state. The X-ray patterns above 1400° C show the crystallization of β-SiC. The crystallite sizes of (1 1 1) at $2\theta = 35.6°$ were estimated using the Scherrer equation to be 0.76, 0.95, 1.34 and 1.48 nm at 1200, 1300, 1400 and 1500° C, respectively. This crystallization is considered to relate to the decrease of the absorption intensity due to the Si–O bond above 1400° C in the infrared spectra of Fig. 3.

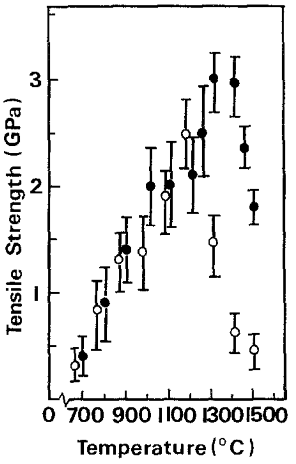

Figure 5 Tensile strength of (●) Si–Ti–C–O fibre and (○) SiC fibre.

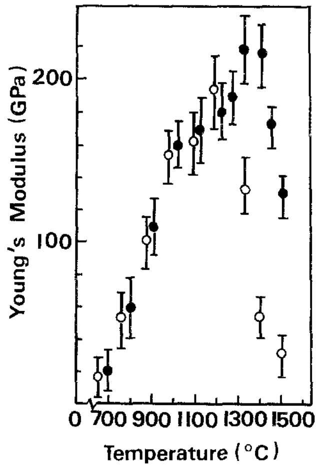

Figure 6 Young's modulus of (●) Si–Ti–C–O fibre and (○) SiC fibre.

Figs 5 and 6 show the tensile strength and Young's modulus of the Si–Ti–C–O fibre obtained by the heat treatment of the cured PTC fibre in the temperature range 700 to 1500° C. For reference, those properties of SiC fibre obtained from the cured PC-B fibre are shown together in these figures. The tensile strength and Young's modulus of these fibres increase with heat-treatment temperature. The Si–Ti–C–O fibre and SiC fibre have maximum values at 1300 to 1400° C and 1200° C, respectively. The relation of tensile strength and Young's modulus to the heat treatment in Si–Ti–C–O fibre is very similar to that in SiC fibre, already reported [17, 18]. The mechanical properties of these fibres begin to decrease at a temperature above 1450 and 1300° C, respectively. The decrease of the mechanical properties is considered to be related to the release of oxides with Si–O bonds from the ceramic fibres in Fig. 3, and β-SiC crystallization in Fig. 4. The characteristic feature of Si–Ti–C–O fibre obtained from polytitanocarbosilane consisting of titanium is that the temperature at which its mechanical properties are at a maximum is shifted to a higher temperature from 1200 to 1400° C than those of SiC fibre obtained from polycarbosilane.

The crystal structure and characteristics of Si–Ti–C–O (1300) fibre and SiC (1200) fibre were compared. They were obtained by heat treatment at 1300° C of the cured PTC fibre and at 1200° C of the cured PC-B fibre, respectively.

The density, tensile strength and Young's modulus

TABLE I Chemical compositions (wt %) of Si–Ti–C–O fibre (1300) and SiC fibre (1200)

Sample	Si	C	O	Ti	B	N
Si–Ti–C–O (1300)	51.0	27.9	17.7	3.1	0.02	0.1
SiC fibre (1200)	56.5	28.2	15.1	–	0.03	0.1

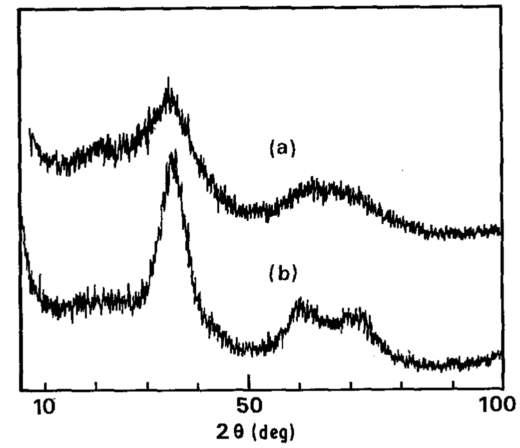

Figure 7 X-ray diffraction patterns of (a) Si–Ti–C–O fibre (1300) and (b) SiC fibre (1200).

of Si–Ti–C–O (1300) fibre and SiC (1200) fibre were 2.35 g cm^{-3}, 3.0 ± 0.2 and 220 ± 10 GPa, and 2.55 g cm^{-3}, 2.5 ± 0.3 and 190 ± 15 GPa, respectively. The specific strength and specific modulus of their fibres were 130 and 9546 km, and 100 and 7600 km, respectively. Thus the mechanical properties of the former are superior to those of the latter, for use as reinforcement fibre of light structural composite materials.

The results of chemical analysis, X-ray diffraction patterns and high-resolution electron micrographs of Si–Ti–C–O (1300) fibre and SiC (1200) fibre are shown in Table I, Figs 7, 8a and b, respectively. The Si–Ti–C–O (1300) fibre and SiC (1200) fibre are considered to be in the amorphous state consisting of silicon, carbon, oxygen, titanium, a trace amount of boron and nitrogen, and β-SiC microcrystalline state respectively. In Fig. 8a, the lattice image corresponding to a 0.25 nm interlayer spacing of β-SiC (1 1 1) planes is observed in some areas of the Si–Ti–C–O (1300) fibre and its size is less than 2 nm. On the other hand, in Fig. 8b, the lattice image is observed in all areas of SiC (1300) fibre and its size is 3 to 4 nm. It is clear from these results that Si–Ti–C–O fibre retains the amorphous state up to 1300° C but SiC fibre is a uniform dispersion of β-SiC microcrystallites at 1200° C. The heat-treatment temperature of Si–Ti–C–O fibre with maximum mechanical strength shifted to a higher temperature than that of SiC fibre as shown in Figs 5 and 6, and the above difference of microcrystalline structure in both fibres is considered to be related to this shifting.

TABLE II The relationship between the mechanical strength and the specific resistances of Si–Ti–C–O fibre

Type	Specific resistance (Ω cm)	Tensile strength (GPa)	Young's modulus (GPa)
A	10^6–10^7	1.8–2.0	160–170
B	10^5–10^6	2.0–2.5	170–190
C	10^4–10^5	2.5–2.8	190–200
D	10^3–10^4	2.8–3.0	200–220
E	10^2–10^3	2.8–3.0	200–220
F	10^1–10^2	2.8–3.0	200–220
G	10^0–10^1	2.8–3.0	200–220
H	10^{-1}–10^0	2.8–3.0	200–220

Fig. 9 shows the changes in the tensile strength of Si–Ti–C–O fibre, carbon fibre, SiC fibre and SiC/C fibre (AVCO, USA, SCS-2) after heat treating at 400 to 1300° C in air for 1 h. Si–Ti–C–O fibre has a higher heat resistance, which may be available for

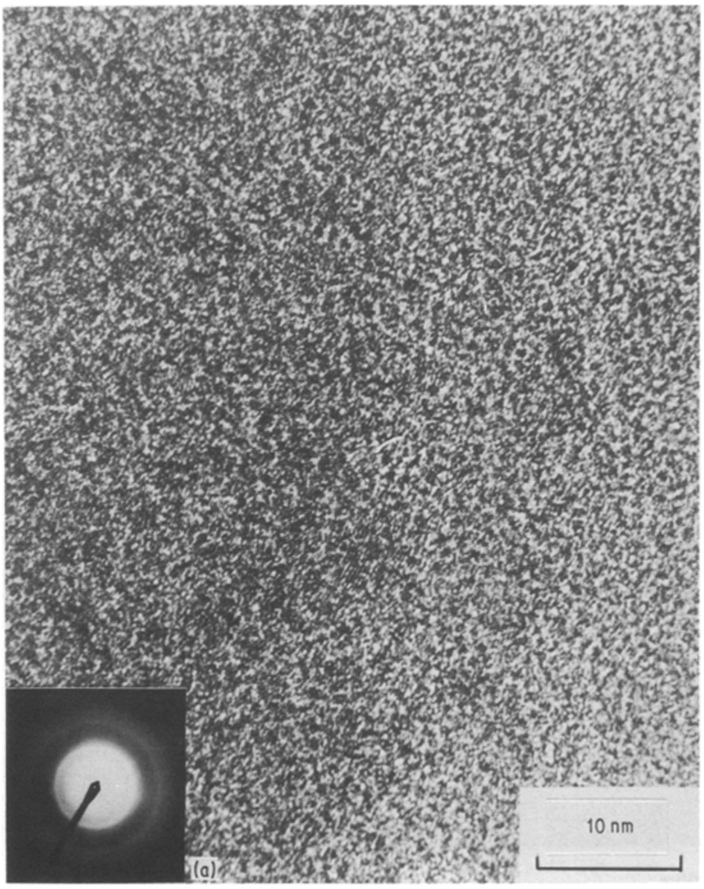

Figure 8 High-resolution electron micrographs of (a) Si–Ti–C–O fibre (1300) and (b) SiC fibre (1300).

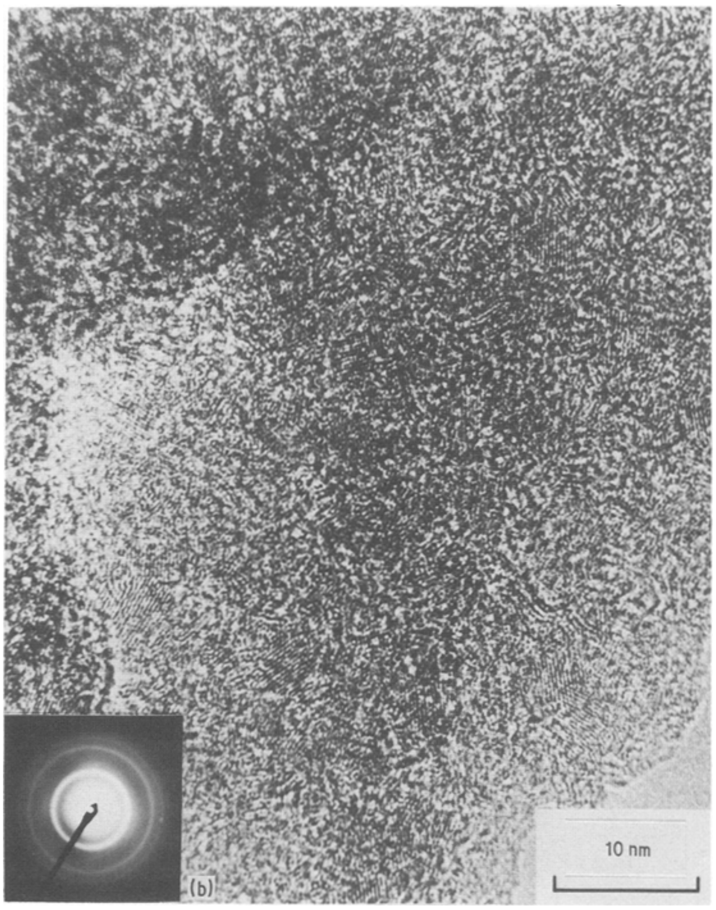

Figure 8 Continued.

obtaining ceramic matrix composites, than SiC fibre and SiC/C fibre. The fall in the mechanical strength of Si–Ti–C–O fibre and SiC fibre above 1300 and 1100° C, respectively, occurs by the elimination of carbon from the fibre and the formation of silicon oxide on the surface of the fibre. This superior heat resistance of Si–Ti–C–O fibre to SiC fibre may be ascribed to the bonding of nonstoichiometric excess carbon with titanium or the increase in the overall bonding strength of the constituent elements in the fibre by addition of titanium.

As shown in Table II, Si–Ti–C–O fibres ranging in specific resistance from 10^7 to $10^{-1}\,\Omega$cm can be arbitrarily produced by changing the component in the fibre or controlling the production process of the fibre. These fibres can be used as special plastic matrix composites; for example, the microwave absorbable or permeable materials, different from those hitherto developed composites using carbon fibre or glass fibre.

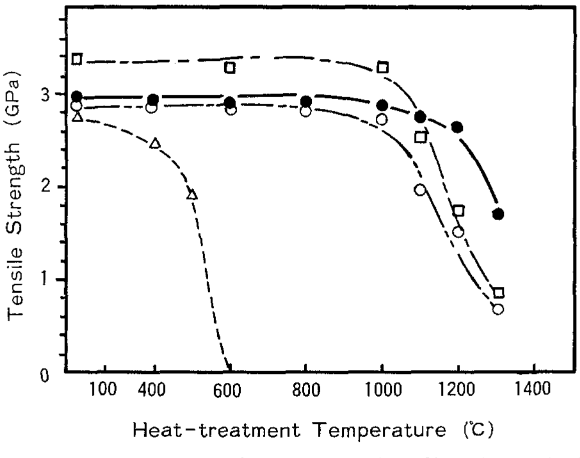

Figure 9 Heat resistance of (– – △ – –) carbon fibre, (— ○ – –) SiC fibre, (— □ – –) SiC/C fibre, and (— ● —) Si–Ti–C–O fibre (1300).

4. Conclusion

Polytitanocarbosilane has been prepared on an industrial scale as a useful precursor for a ceramic fibre. This polymer is easily spun, and Si–Ti–C–O ceramic fibre was continuously synthesized from the melt-spun polymer fibre. The heat-treatment temperature (1400° C) for preparing Si–Ti–C–O fibre of maximum mechanical properties shifted to a higher temperature than that (1200° C) of SiC fibre. This shift may be attributed to the retention of the amorphous state in Si–Ti–C–O fibre at the higher temperature in comparison with that of SiC fibre.

The Si–Ti–C–O fibre obtained from polytitanocarbosilane containing titanium had higher specific strength, specific Young's modulus, heat resistance and specific resistance ranging from 10^7 to $10^{-1}\,\Omega$cm in comparison with those of SiC fibre. It is considered that the Si–Ti–C–O fibre is very useful as a reinforcement fibre of composite materials.

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Received 10 August
and accepted 22 October 1987