JOURNAL OF MATERIALS SCIENCE 31 (1996) 3231–3235

Characteristics of a continuous Si–Ti–C–O fibre with low oxygen content using an organometallic polymer precursor

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A continuous Si–Ti–C–O fibre with 12 wt% oxygen content, which is lower than the usual 18 wt% found in the normal fibres, was synthesized by using polytitanocarbosilane which has fewer Si–Si bonds than the usual precursor polymer. The density, tensile strength, tensile modulus and thermal conductivity were found to be 2.37 g cm^{-3}, 3.4 ± 0.3 GPa, 190 ± 10 GPa and 1.40 W m^{-1} K^{-1}, respectively. Amongst these properties, the tensile modulus was improved by 20 GPa and the thermal conductivity had a higher value in comparison with that of the ordinary Si–Ti–C–O fibre with 18 wt% oxygen content. The Si–Ti–C–O fibre with a 12 wt% oxygen content has a better heat resistance above 1400 °C in an argon atmosphere and 1300 °C in air, than the usual fibre. About 60 and 40% of its tensile strength at room temperature were retained in air at respectively, 1500 and 1600 °C. This improved ceramic fibre is considered to be useful as a reinforcing material for advanced composites such as high-temperature ceramic matrix composites and metal matrix composites.

1. Introduction

An organometallic polymer, polytitanocarbosilane, which can be converted by pyrolysis into a mixture of silicon carbide and titanium carbide with a high yield, has been prepared from polydimethylsilane and titanium tetrabutoxide in the presence of a small amount of polyborodiphenylsiloxane [1]. This polytitanocarbosilane is formed by the cross-linking of polycarbosilane with titanium compounds [1]. Using this polymer, a Si–Ti–C–O fibre (Tyranno Fibre®) with good mechanical properties and excellent heat resistance has been synthesized from the melt-spun polytitanocarbosilane fibre by curing in air and then heat-treating in an inert gas atmosphere [2, 3].

The heat-treatment temperature (1300–1400 °C) in an inert gas atmosphere for the preparation of a Si–Ti–C–O fibre with maximum mechanical properties is at a higher temperature compared to that for a SiC fibre (1200 °C) obtained from polycarbosilane [3]. This shift is attributed to the retention of the amorphous state in the Si–Ti–C–O fibre at higher temperatures compared to that in the SiC fibre. Titanium compounds in the Si–Ti–C–O fibre play an important role in controlling the crystalline grain growth up to the high temperature [3]. A Si–Ti–C–O fibre also has a higher heat resistance in air than SiC, SiC/C and carbon fibre, which find application in ceramic matrix composites [3]. In addition Si–Ti–C–O fibres ranging in specific resistance from 10^6 to 10^0 Ω cm can be produced by either changing the components in the fibre or by controlling the production process [3, 4].

In spite of its widespread use in plastic matrix composites, metal matrix composites and ceramic matrix composites [4–9] the Si–Ti–C–O fibre material requires further improvement in respect to its heat resistance if it is to be applied successfully as a high-temperature structural material.

From the investigation of new organometallic polymers and their fibres, a new type of Si–Ti–C–O fibre with a lower oxygen content and higher heat resistance than that of the ordinary fibre has been prepared. The synthesis method and characteristics of this fibre are presented in this paper.

2. Experimental procedure

2.1. Synthesis of polytitanocarbosilanes and Si–Ti–C–O fibres

Two types of polytitanocarbosilanes, PTC1 and PTC2, were prepared as the precursors for the Si–Ti–C–O fibres. The PTCs were synthesized by the reaction of polydimethylsilane (PS) with titanium tetrabutoxide (TBT) in the presence of a small amount of polyborodiphenylsiloxane (PBDS) under a nitrogen atmosphere. The reaction conditions are shown in Table I. Larger amounts of PBDS were used as a catalyst for the synthesis of PTC1, and the reaction temperature for the synthesis of PTC2 was consequently higher than that of PTC1. The polymers were concentrated at 320 °C for 2 h in a nitrogen flow in order to remove the low molecular weight, materials which cause melting and agglomeration of the spun fibres during curing.

0022–2461

TABLE I Properties of Si–Ti–C–O fibres

Polytitanocarbosilane		PTC1	PTC2
Quantity of PS	(kg)	100	100
PBDS	(kg)	3	0.5
TBT	(kg)	10	10
Reaction temperature	(°C)	340	380
Reaction time	(h)	12	12

PTC1 and PTC2 were melt-spun between 220–240 °C using a multiple-hole nozzle and wound on to the drum at about a 600 m min^{-1} drawing speed. Afterwards the spun PTC1 and PTC2 fibres were cured in air in the range 160–220 °C for 3 h at a heating rate of 10 °C h^{-1}, the cured PTC fibres were heat-treated continuously at 1300 °C in a nitrogen flow to obtain continuous Si–Ti–C–O fibres, TF1 and TF2. The oxygen content in TF1 and TF2, which were controlled by changing the curing conditions, were 14–25 and 8–18 wt %, respectively.

2.2. Measurements

Gel-permeation chromatograms (GPC) were taken with a Toyo Soda HCL–801A, with G–4000 HXL, G–3000 HXL, G–2000 HXL (× 2) and G–2000 H8 (× 2) packing and tetrahydrofran eluent at a flow rate of 1 cm^3 min^{-1} at 40 °C using polystyrene as a standard specimen. X-ray diffraction patterns of pulverized Si–Ti–C–O fibres were recorded with Rigaku X-ray diffractometer using CuK$_\alpha$ radiation with a nickel filter.

Ultraviolet spectra were measured in a 0.02 g dm^{-3} n-hexane solution with a Shimadzu UV–2100 using a 1 cm light-path length in the solution cell. The absorptivities of the specimens were calculated from the following equation.

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

where K is the absorptivity (dm^3 g^{-1} cm^{-1}), C the concentration (g dm^{-3}), L the light-path (cm), $\log(I_0/I)$ the absorbance.

The density of the fibres were measured using a density gradient tube with carbon tetrachloride and bromoform as the immersion liquids.

The thermal conductivity of the fibres were calculated from the following equation.

$$\lambda = 418.4\,\alpha\,\rho\,C_p$$

where λ is the thermal conductivity (W m^{-1} K^{-1}), α the thermal diffusibility of the fibres (cm^2 s^{-1}), which were measured by ac calorimetry with a Shinku Riko PIT–1 under vacuum, ρ the density of the fibres (g cm^{-3}), C_p the specific heat (cal/g/°C) measured by the differential scanning calorimeter method with a Perkin–Elmer DSC–2.

The tensile strength and tensile modulus of Si–Ti–C–O fibres were measured using two universal testing machines: one was a Tosoku Measuring Instruments Tensilon CFT–200 used for the strand method (150 mm gauge length and 60 mm min^{-1} cross head speed at room temperature), the other was an Orientech Tensilon UTM–II used for the monofilament method (25 mm gauge length and 2 mm min^{-1} cross head speed at room temperature, 100 mm gauge length and 4 mm min^{-1} cross head speed at 1200–1600 °C in air).

3. Results and discussion

The tensile strength and the tensile modulus of a Si–Ti–C–O fibre begin to drop at temperatures above 1400 °C in an argon atmosphere and above 1300 °C in air. This decrease in the mechanical properties is thought to be related to the release of carbon, silicon and oxygen atoms from the fibre as carbon monoxide or dioxide and silicon oxides, followed by the crystalline grain growth of β-SiC in the fibre [2, 3]. One of the most obvious means of improving the heat resistance of the Si–Ti–C–O fibre if it is to be used as a high-temperature structural material seems, therefore, to be to lower the oxygen content in the fibre.

The oxygen content in the Si–Ti–C–O fibres is mainly determined by the curing treatment in air imposed on the PTC fibres, and so it can be varied by controlling the conditions in the curing process. Fig. 1 shows the relationship between the mechanical properties, the tensile strength and the tensile modulus, and the oxygen content in Si–Ti–C–O fibres (TF1) which were obtained by curing spun PTC1 fibres at 160, 175, 190, 205 and 220 °C in air, and then heat-treating at 1300 °C in a stream of nitrogen. The tensile strength and the tensile modulus of a fibre with about 18 wt % oxygen content have maximum values. Above this oxygen content the mechanical properties drop gradually as the oxygen content increases. An abrupt decrease in the mechanical strengths of the fibre below 15 wt % oxygen content is attributed to partial melting followed by agglomeration of the fibres obtained by heat-treatment. As seen from these results, it is difficult to reduce the oxygen content in the fibre to less than 15 wt % by controlling the curing conditions without lowering mechanical properties if PTC1 is selected as the precursor polymer for the fibre. It is

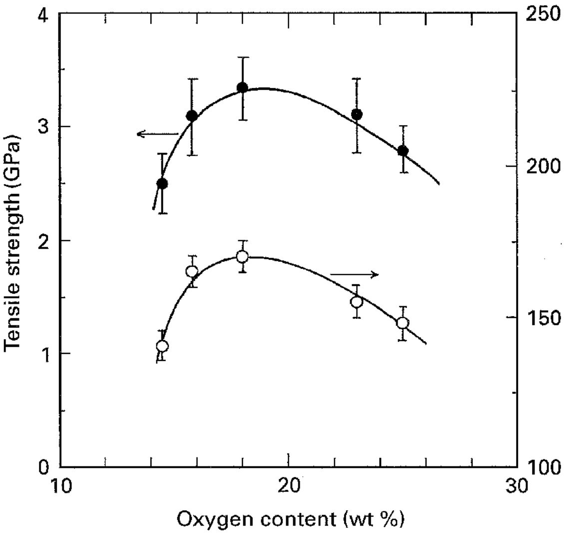

Figure 1 Relationship between the mechanical properties and oxygen content in Si–Ti–C–O fibres prepared from PTC1.

necessary therefore to change the PTC's structure if we are to obtain a fibre with both a low oxygen content and a high mechanical strength.

Two reactions occur in the curing process. The dominant reaction shown in Equation 1, produces cross linked structures comprising of Si–O–Si bonds by the reaction of Si–H bonds in the PTC with oxygen from the air. This reaction is accompanied by a minor parasitic reaction which is shown in Equation 2. If we are to develop low oxygen content fibres then we must control the reaction of Equation 1. The key to understanding the reaction is to realize that the binding energy of Si–Si bonds is lower than that of Si–H bonds and that consequently the oxygen atoms will be preferentially inserted into the Si–Si bonds rather than the Si–H bonds. Therefore one strategy towards obtaining low oxygen content fibres will be the use of a PTC with as few Si–Si bonds as possible.

$$2\ \mathrm{CH_3} - \overset{|}{\underset{|}{\mathrm{Si}}} - \mathrm{H} + \mathrm{O_2} \rightarrow$$

$$\mathrm{CH_3} - \overset{|}{\underset{|}{\mathrm{Si}}} - \mathrm{O} - \overset{|}{\underset{|}{\mathrm{Si}}} - \mathrm{CH_3} + \mathrm{H_2O} \qquad (1)$$

$$- \overset{|}{\underset{|}{\mathrm{Si}}} - \overset{|}{\underset{|}{\mathrm{Si}}} - \ + 1/2\ \mathrm{O_2} \rightarrow\ - \overset{|}{\underset{|}{\mathrm{Si}}} - \mathrm{O} - \overset{|}{\underset{|}{\mathrm{Si}}} - \qquad (2)$$

In the synthesis of PTC, PBDS is considered to play a role in accelerating the polycondensation reaction by dehydrogenation of Si–H bonds with the formation of Si–Si bonds [10]. PTC2 was, therefore, synthesized in the presence of 0.5 wt % PBDS, as shown in Table I which is significantly smaller than the 3 wt % found with the ordinary precursor polymer, PTC1. In addition, its synthesis was carried out at a high temperature, 380 °C, which is a more advantageous temperature for lowering residual Si–Si bonds than the 340 °C used in the synthesis of PTC1. Fig. 2 shows GPC curves for PTC1 and PTC2. The number-average molecular weight, Mn of PTC2 is 750, which is a little smaller than that of PTC1. The Mw/Mn of PTC2 and PTC1 are 2.60 and 2.80, respectively (Mw: weight–average molecular weight), and thus, the molecular weight distribution of PTC2 is sharper than that of PTC1. These results for PTC2 are ascribed to the depression of the polycondensation reaction by the dehydrogenation of Si–H bonds in the presence of a small amount of PBDS. The number of Si–Si bonds in PTC2 is also observed to considerably decrease in comparison with those in PTC1 as seen from the absorption peaks at 210 nm in the ultraviolet spectra which correspond to the Si–Si bond (Fig. 3).

The relationship between the oxygen content and the mechanical properties of Si–Ti–C–O fibres obtained by heat-treating PTC2 spun fibres cured under different conditions at 1300 °C in nitrogen atmosphere are shown in Fig. 4. The tensile strength and the tensile modulus of the Si–Ti–C–O fibre with 12 wt % oxygen content, which is 6 wt % lower than that from using PTC1, have maximum values. This phenomena

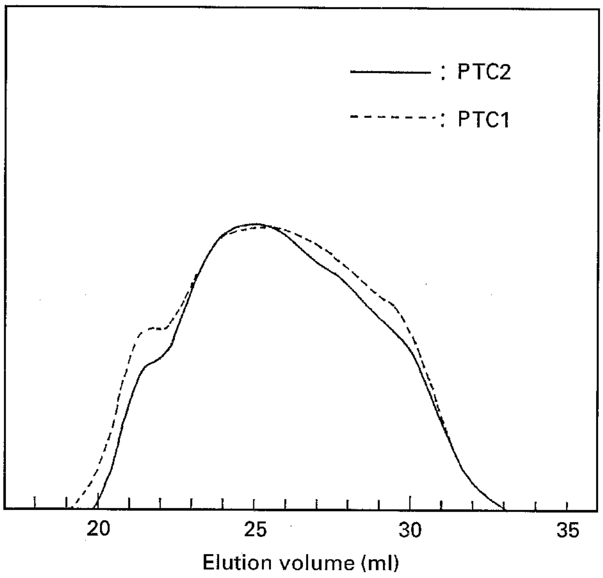

Figure 2 GPC curves of PTC1 and PTC2.

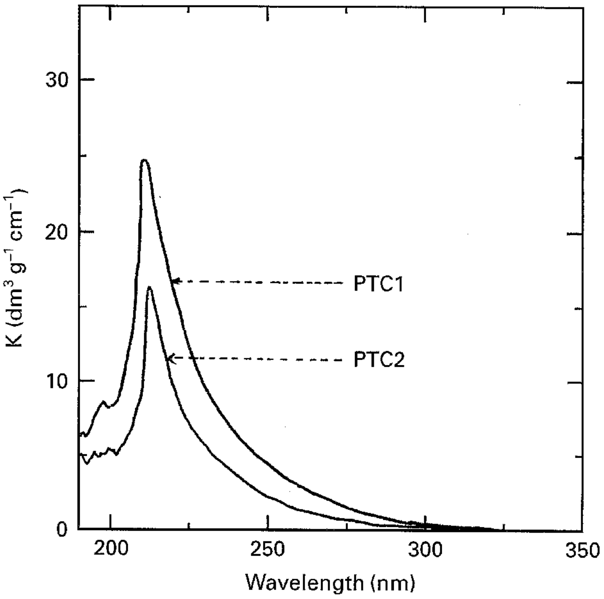

Figure 3 UV spectra of PTC1 and PTC2 solution.

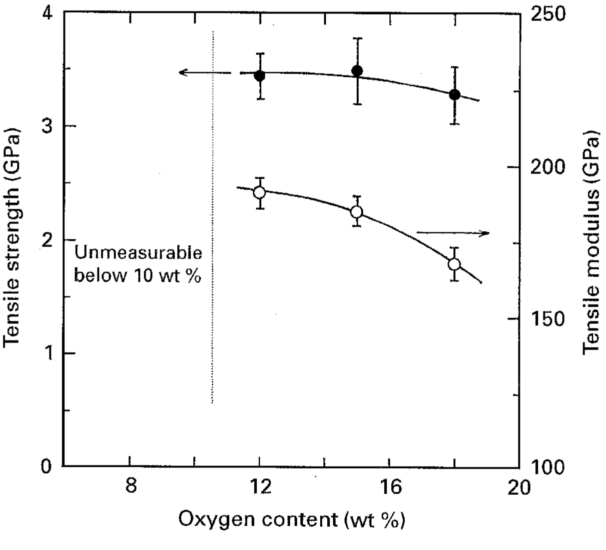

Figure 4 Relationship between mechanical properties and oxygen content in Si–Ti–C–O fibres prepared from PTC2.

is assumed to be due to fewer Si–Si bonds in PTC2 than in PTC1 and a consequent depression of the insertion of oxygen atoms in the PTC2 main-chains during the curing process. The Si–Ti–C–O fibres with less than 10 wt % oxygen content partially melt and attach to each other, so that their mechanical properties are unmeasurable.

The properties of the Si–Ti–C–O fibres (TF1(18) and TF2 (12)) with 18 wt % and 12 wt % oxygen contents using PTC1 and PTC2 as precursor polymers, respectively, are summarized in Table II. The tensile strengths of both fibres are the same, whereas the tensile modulus of TF2 (12) is increased by 20 GPa compared with that of TF1 (18). The thermal conductivity of TF2 (12) also shows a higher value than that of TF1 (18).

In the X-ray powder diffraction patterns of TF1(18) and TF2 (12), as shown in Fig. 5, the apparent crystalline sizes of TF1(18) and TF2 (12) calculated from the (111) diffraction intensity of the β-SiC-type phase appearing at $2\theta = 35.8°$ are 1.0 and 1.2 nm, respectively, and it is obvious that TF1 (18) is a more amorphous material than TF2 (12). The reason why TF2 (12) has the higher tensile modulus, density and thermal conductivity than TF1(18), consequently, appears to be attributed to the difference in the crystalline size of the fibres.

Fig. 6 shows the tensile strengths of TF1 (18) and TF2 (12) after heat-treatment at a temperature range of 1000–1500 °C for 1 h in an argon atmosphere. In order to confirm whether the difference in heat resistance between TF1 (18) and TF2 (12) is dependent upon the structure of the precursor polymer itself or the oxygen content in the fibre, the heat resistance of the Si–Ti–C–O fibre with 18 wt % oxygen content (TF2 (18)) using PTC2 as a precursor polymer prepared by changing the curing conditions is also given in Fig. 6. The tensile strengths of the three fibres are constant up to 1300 °C, but drop above 1400 °C. The residual mechanical strength of TF2 (12) after heat-treatment at high temperatures above 1400 °C is the highest amongst the three types of fibres, and this fibre keeps 2 GPa of its tensile strength after heat-treatment even at 1500 °C. The mechanical strengths of TF1 (18) and TF2 (18) decrease enormously after heat-treatment above 1400 °C. From these results, it is clear that

TABLE II The reaction conditions of PTCs

Si–Ti–C–O Fibre		TF1(18)	TF2(12)
Oxygen content	(wt %)	18	12
Average diameter	(μm)	8.5	8.5
Tensile strength	(GPa)	3.3 ± 0.3	3.3 ± 0.3
Tensile modulus	(GPa)	170 ± 10	190 ± 10
Elongation at break	(%)	2.0	1.8
Density	(g/cm^3)	2.35	2.37
Thermal conductivity	(W/m/K)	0.97	1.40

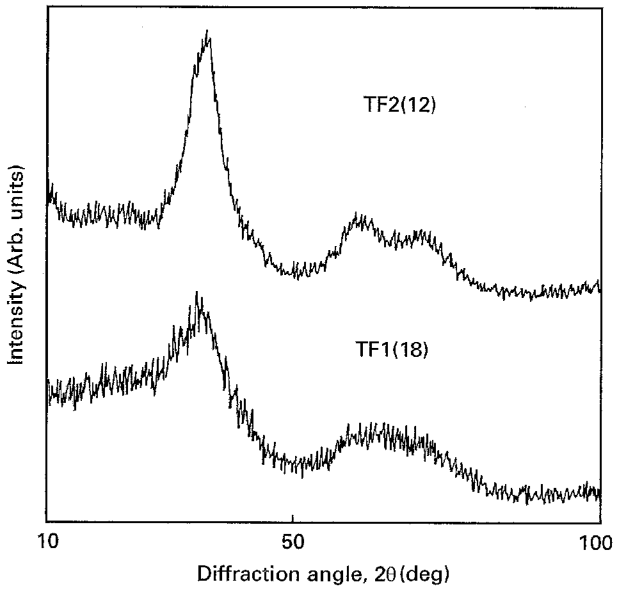

Figure 5 X-ray diffraction patterns of TF1 (18) and TF2 (12).

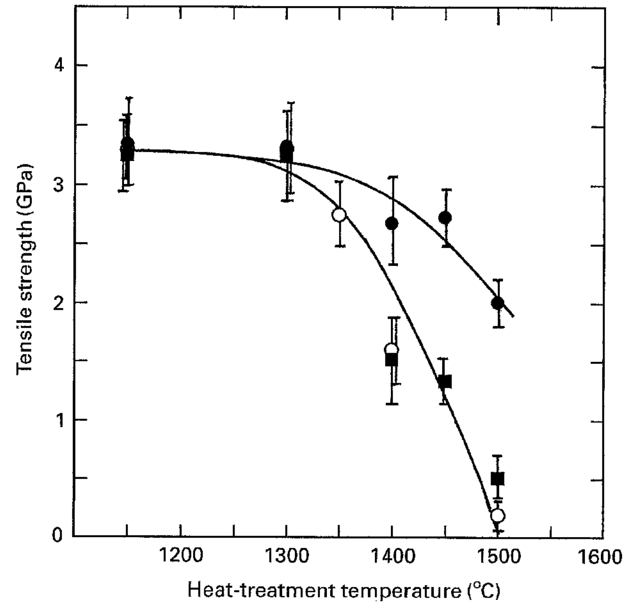

Figure 6 Tensile strengths of (●) TF2 (12), (○) TF1 (18) and (■) TF2 (18) after heat-treatment in argon for 1 h.

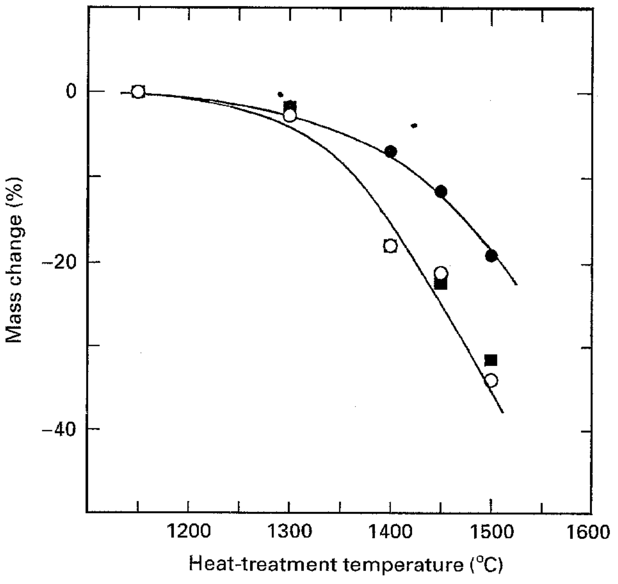

Figure 7 Mass change of; (●) TF2 (12), (○) TF1 (18) and (■) TF2 (18) after heat-treatment in argon for 1 h.

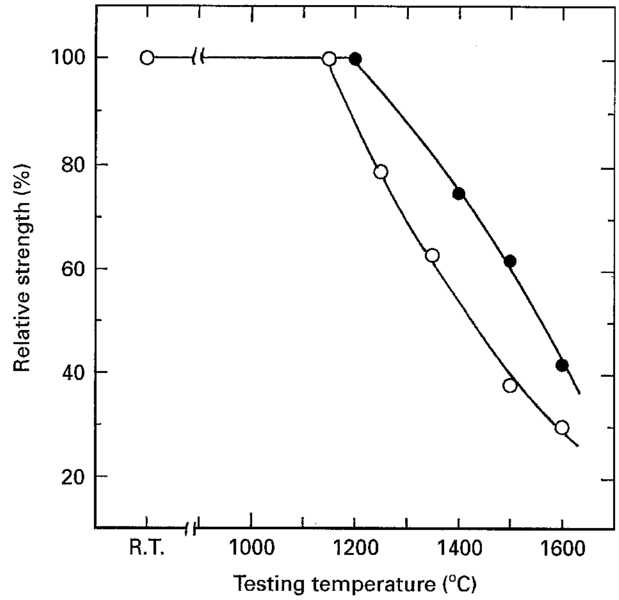

Figure 8 Relative tensile strength of (●) TF2 (12) and (○) TF1 (18) at high temperature in air.

the introduction of excess oxygen into the PTC2 spun fibre lowers the heat-resistance though TF2 (12) obtained from a PTC2 fibre, which is cured by forming the cross-linked structure, shows high heat resistance. The heat resistance results of the three fibres are in fairly good agreement with the measured mass changes in the same temperature range as is shown in Fig. 7.

The relative tensile strengths of TF1(18) and TF2 (12) at temperatures from 1200–1600 °C in air to their strength at room temperature are shown in Fig. 8. No drops in the mechanical properties of the two fibres are observed up to 1200 °C, but the mechanical strength decreases gradually above 1300 °C as the temperature is raised. The oxidative heat resistance of TF2 (12) is also superior to that of TF1(18), and TF2 (12) retains about 60 and about 40 % of the relative strength at 1500 and 1600 °C, respectively, to the strength at room temperature.

4. Conclusions

A polytitanocarbosilane containing fewer Si–Si bonds (PTC2) was obtained from polydimethylsilane and titanium tetrabutoxide in the presence of a lower amount of polyborodiphenylsiloxane at a higher temperature than that found in the synthesis of ordinary polytitanocarbosilane (PTC1). A Si–Ti–C–O fibre with 12 wt % oxygen content (TF2 (12)), was synthesized from the PTC2 melt-spun fibre by pyrolysis at 1300 °C in an inert gas atmosphere. It has higher mechanical properties, especially a higher tensile modulus and a better heat resistance above 1400 °C in argon and 1300 °C air, than that of the ordinary Si–Ti–C–O fibre with 18 wt % oxygen content (TF1 (18)), obtained from the PTC1 melt-spun fibre. This new fibre, TF2 (12), has advantages for application in advanced composites, such as, ceramic matrix composites and metal matrix composites applicable to high-temperature and high-performance structural materials.

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Received 21 March
and accepted 15 December 1995