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Tensile testing at high temperatures of ex-PCS Si–C–O and ex-PCSZ Si–C–N single filaments

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A microtensile tester consisting mainly of an induction-heated furnace, a 0–2 N load cell, a 0.1/1 μm sensitivity straining device and hot grips has been designed and used to test ceramic single ceramic filaments at 25–1600 °C under vacuum (0.1 Pa) or in controlled atmospheres. Both failure strength and Young's modulus were measured with an isothermal gauge length of 30 mm. A system compliance correction was applied for each test temperature and material. The apparatus was used to characterize an ex-poly-carbosilane Si–C–O fibre (Nicalon NLM-202) and an ex-polycarbosilazane Si–C–N experimental single filament almost free of oxygen (γ-ray curing). Both materials exhibit a significant strength loss at 1200–1600 °C when tested under vacuum, assigned to a decomposition process with an evolution of gaseous species (SiO/CO or N_2) and the formation of a mechanically weak decomposition surface layer. Conversely, the Si–C–N filament undergoes no strength loss when tested in an atmosphere of nitrogen ($P = 100$ kPa) at 1200 °C, the decomposition being impeded by the external nitrogen pressure. In all cases, no significant decrease in Young's modulus was observed.

1. Introduction

Ceramic matrix composites (CMCs) have been designed mainly for use at high temperatures. They consist of ceramic fibres embedded in a ceramic matrix (e.g. glass–ceramic, oxide or carbide) according to a gas or liquid phase route. CMCs exhibit, with respect to monolithic ceramics, a significantly improved toughness and reliability when the fibre–matrix bonding has been properly controlled during processing (i.e. when a compliant interphase is present at the fibre–matrix interface) [1].

A number of ceramic matrices, including SiC, Si_3N_4, Al_2O_3, stabilized zirconia, or glass–ceramics, could undergo long exposures at temperatures of at least 1400 °C in oxidizing atmospheres, without any significant damage. Unfortunately, the situation is less satisfactory for the fibres. Carbon fibres, which have probably the highest potential in this field (in terms of strength and stiffness), are sensitive to oxygen at low temperatures. Polycrystalline oxide fibres (e.g. Al_2O_3–SiO_2, pure alumina, tetragonal or cubic $ZrO_2(Y_2O_3)$), which are by nature, insensitive to oxidation are not stable, from a microstructural standpoint, beyond about 1000 °C (grain growth phenomenon). Finally, a variety of ceramic fibres have been prepared in the Si–C–O, Si–C–N and Si–C–N–O systems from organosilicon polymeric precursors, according to a spinning–curing–pyrolysis process. These fibres are either amorphous or poorly crystallized depending on their chemical composition and pyrolysis temperature. The most commonly used in CMCs, the Si–C–O fibres obtained from the pyrolysis at 1100–1300 °C of an oxygen-cured polycarbosilane (PCS) precursor (Nicalon fibres from Nippon Carbon), are known to undergo a decomposition process with an evolution of gaseous species (i.e. CO and SiO), the formation of residual porosity, free carbon and crystalline phases (such as SiC) [2]. This decomposition process is already effective at 1100 °C and results in a dramatic decrease in the mechanical properties of the material [3].

The mechanical testing of brittle fibres on monofilament specimens (whose diameters are in the range 7–20 μm) is difficult even when performed at room temperature. Moreover, an accurate characterization of the fibre strength requires a large number of tests owing to the statistical character of the failure of ceramic materials [4–7]. Most studies reported up to now, with a view to assessing the high-temperature potential of ceramic fibres, have been limited to annealing treatments performed under various conditions (in terms of temperature, atmosphere and duration) and followed by mechanical testing at room temperature [3, 8–12]. As a matter of fact, very few data are available from the literature on the high-temperature mechanical properties of ceramic fibres [13–17]. One of the most recent and complete studies is that of Pysher and co-workers [14, 16] on the measurement of the tensile strength and stiffness in air of various oxide and non-oxide fibres within the temperature range 25–1400 °C. Furthermore, in many high-temperature mechanical testing experiments,

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only part of the fibre length is heated (in order to use cold grips) thus rendering difficult the accurate measurement of the high-temperature Young's modulus.

The present work, which is part of a more general research programme on ceramic fibres and CMCs, had two objectives: (i) the first and main objective was to set up a microtensile device which could be used to test at high temperatures (up to about 1700 °C) existing or experimental fibres in a vacuum or controlled atmospheres, the fibre specimen being entirely heated at the test temperature (in order to assess the high temperature Young's modulus); and (ii) the second objective was to study the effect of the test atmosphere on a few ceramic fibres prepared from organosilicon precursors.

2. Experimental procedure

2.1. Materials

Two different materials have been used in the present work, either to validate the microtensile device using Si–C–O ex-PCS fibre and/or to study the influence of the atmosphere on the high-temperature mechanical properties of the materials (Si–C–O ex-PCS and Si–C–N ex-polycarbosilazane (PCSZ) fibres).

The Si–C–O ex-PCS fibre was a material available from the market (Nicalon NLM-202 ceramic grade from Nippon Carbon). Its preparation from a Yajima-type polycarbosilane precursor has been the subject of many articles [18–20]. It has an overall chemical composition close to 59 wt % Si–31 wt % C–10 wt % O and has been reported to consist of very small β-SiC crystals (a few nanometres in mean size) and some free carbon clusters, both within an amorphous Si–C–O phase [3, 21–23]. Its mean diameter is close to 15 μm (with significant variations both from filament to filament and along the fibre length for a given monofilament). The high-temperature tensile failure strength and Young's modulus of such a fibre have recently been measured, as already mentioned, by Pysher *et al.* [14] up to 1400 °C in air.

The second material was Si–C–N monofilament, prepared on a laboratory scale by Mocaer *et al.* [24, 25] from a polycarbosilazane precursor [24, 25]. The green fibre had been spun, in the molten state, with a spinning device equipped with a single spinneret, cured with γ-rays in argon (in order to avoid the standard oxygen curing step) and finally submitted to a pyrolysis treatment in nitrogen at a temperature of 1200 °C. The overall chemical composition of the Si–C–N filament, i.e. Si 40, C 38, N 19, O 3 at %, corresponds to a formula close to $SiC_{0.93}N_{0.46}O_{0.05}$ which shows the low level of oxygen contamination which has been achieved. The filament has a mean diameter close to 17 μm and is amorphous up to about 1400 °C. Such filament was reported to be microstructurally stable up to 1400–1600 °C in an atmosphere of nitrogen. Furthermore, mechanical tests previously performed at room temperature after annealing treatments in nitrogen showed that the residual Young's modulus was slightly increased and the tensile strength almost unchanged [25]. Conversely, no high-temperature tests have been performed up to now on this promising experimental material.

2.2. Experimental set-up

The experimental set-up, which is shown in Fig. 1, consists of three main parts: (i) a microtensile device which has been previously used for performing mechanical tests at room temperature [4], (ii) an electrical furnace heated by induction and (iii) a vacuum chamber.

The microtensile device consists of a load cell designed and fabricated by SEP, Bordeaux (load range 0–2 N, response 1.7 V N^{-1}, deviation from linearity 0.05%) exhibiting the two following features: (i) its load transducer can be deformed only axially and (ii) it has a high compliance (i.e. 38 μm N^{-1}). The load cell is associated with a straining device (S_2) (model UT 100 CC from Microcontrole) driven at constant speed with a d.c. motor. The displacements are measured with an accuracy of 0.1 or 1 μm through an incremental device mounted directly on the axis of the d.c. motor. The load–displacement curve is obtained with an electronic recorder (model 500 SP from Kontron).

As shown schematically in Fig. 2a, the specimen is heated with an electrical furnace consisting of (i) a graphite susceptor with a hole for a Pt–30Rh/Pt–6Rh type B thermocouple, (ii) a water-cooled induction coil fed with a high-frequency current (N = 138 kHz) delivered by a 3 kW aperiodic power generator (model GHF 3AP from CELES) and (iii) thermal insulation (alumina or/and carbon fibre felts). Additional fibrous thermal protection materials (not shown in Fig. 2a) are set outside the heating element in order to reduce the radial heat flux towards the wall of the vacuum chamber. Such an electrical furnace has several important advantages: (i) very high temperatures (limited presently to 1700 °C by the nature of the thermocouple) can be achieved very easily both under vacuum or in inert atmospheres, (ii) the heating rate is very fast (i.e. of the order of 100 °C min^{-1}), a feature which is of interest to avoid significant decomposition and/or creep of the fibre during heating to test temperature, and (iii) the outgassing of the furnace and hence the contamination of the

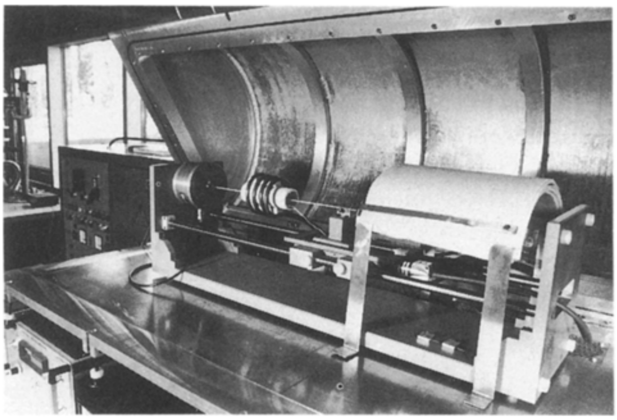

Figure 1 General view of the high-temperature tensile testing device.

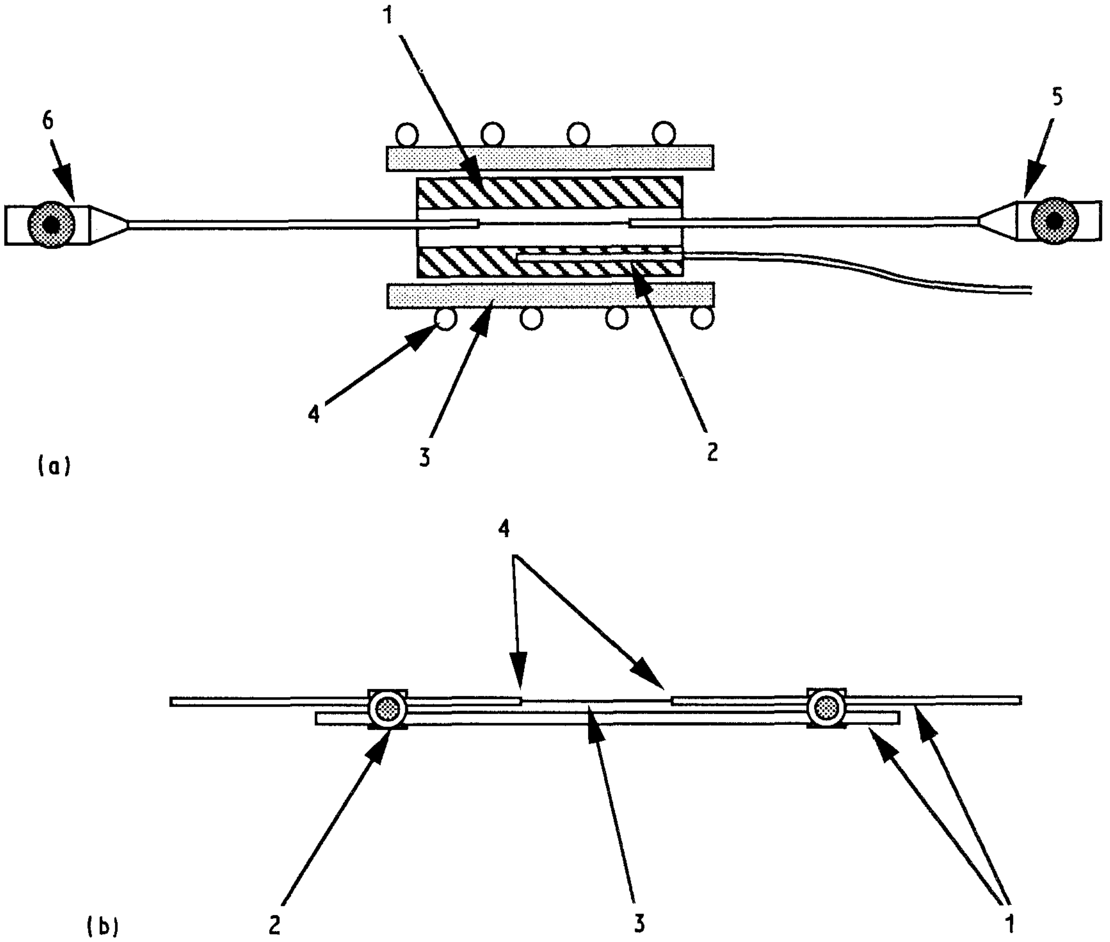

Figure 2 Schematic diagrams of the high-temperature tensile apparatus. (a) The electrical furnace: (1) graphite susceptor, (2) B-type thermocouple, (3) thermal insulation, (4) water-cooled copper induction coil, (5) grip locked with the load-cell, (6) grip locked with the displacement table. (b) Fibre specimen setting: (1) alumina tubes, (2) temporary screw attachment, (3) fibre specimen, (4) high-temperature joints between the fibre and the alumina tubes.

atmosphere and specimen during the high-temperature tensile test is reduced. Finally, a temperature profiling of the hot zone has been done with a thermocouple mounted on the displacement table and translated along the axis of the cylindrical hot zone under constant heating power (Fig. 3), with the following main results: (i) the axial temperature profile is roughly symmetrical with respect to the induction coil centre, as could be expected, (ii) within a central length of 30 mm and for a test temperature of about 1400 °C the temperature can be considered as constant at ± 7 °C, and (iii) the temperatures measured by the thermocouple in the graphite susceptor and that measured by the thermocouple set in the axis of the hot zone are the same for the heating rate mentioned above.

The last part of the apparatus is a hemi-cylindrical vacuum chamber which consists of a flat aluminium base (thickness 20 mm, rubber O-ring joint) and an aluminium cover (thickness 6 mm, three stiffeners). It can be maintained either under vacuum (with a turbomolecular pump (model PT 50 from Leybold); residual pressure less than 0.1 Pa (10^{-3} torr)) or under an inert atmosphere (e.g. argon or nitrogen at $P = 100$ kPa). Residual pressure is measured with two gauges (Pirani-type for primary vacuum and cold-cathode gauge for secondary vacuum).

2.3. Test procedure

The main features of the experimental procedure selected result directly from the choice which has been made to heat the entire fibre specimen at the test temperature, i.e. to use high-temperature "grips".

As shown schematically in Fig. 2b, the fibre specimen is attached at both ends to alumina tubes (length 200 mm, outer diameter 2 mm, inner diameter 1 mm) with a two-constituent high-temperature cement (over a length of about 10 mm to achieve a high strength/stiffness joint). After several attempts, a magnesia-based cement (Ceramabond 571 from Aremco Products) was selected on the basis of the following features: (i) the high coefficient of thermal expansion (CTE) of magnesia, i.e. $12.6 \times 10^{-6}\,°\mathrm{C}^{-1}$ with respect to that of the alumina holders ($8.1 \times 10^{-6}\,°\mathrm{C}^{-1}$) clamps the fibre specimen in the alumina tube when the joints are heated at high temperatures, thus preventing sliding under loading (such sliding has actually been observed when different cements were used); (ii) the ability to select the proper ratio between the two constituents of the cement, i.e. the magnesia powder and the polymeric resin, in order to achieve a mixture fluidity compatible with a capillary ascent in the alumina tube holders; and (iii) the high value of its maximum use temperature (i.e. about 1760 °C).

The specimen–alumina tube assembly is maintained aligned temporarily with a third alumina rod, as schematically shown in Fig. 2b, in order to measure: (i) the gauge length with a cathetometer (Wild Leitz) (the gauge length was limited to 30 mm as discussed in section 2.2 and shown in Figs 2a and 3, and measured with an accuracy of 10^{-1} mm); and (ii) the fibre diameter according to a laser diffraction technique (three measurements performed near each end and the centre) and a correction taking into account both the deviation from cylindricity and optical properties of the material [26].

One of the alumina tube holders is rigidly locked with the displacement motor-driven table and the table carriage is moved to let the whole specimen–alumina holder assembly pass through the graphite susceptor of the electrical furnace. The second alumina tube holder is then locked with the load-cell and finally, the third alumina holder is removed.

The chamber is first evacuated down to 0.1 Pa (which requires about 2 h) and then either maintained under vacuum or filled with an inert gas (pure argon or nitrogen at a pressure of 100 kPa) depending on the nature of the test. The temperature is raised at a rate of 100 °C min^{-1} (this value has been established empirically as that necessary to achieve thermal equilibrium) up to the test temperature, the mechanical tensile testing (which requires by itself only a few seconds) being performed as soon as the test temperature is reached.

The ex-PCS Si–C–O fibres were tested under vacuum at 800, 1100 and 1400 °C since data were already available in the literature for tests performed in air or argon at 100 kPa [13, 14], on the one hand, and since these fibres were reported to undergo a decomposition process whose effect on their mechanical properties could be enhanced under vacuum [3, 7–11], on the other hand. For a given temperature, the experiments were considered satisfactory when a minimum of five monofilament specimens yielded simultaneous measurements of both Young's modulus and ultimate failure stress. Additional experiments were performed at 600 °C but used only for the measurement of the Young's modulus, as discussed in the next section. The ex-PCSZ Si–C–N–O fibres were tested only at 1200 °C (i.e. their processing temperature) owing to the limited amount of material available [25].

The ultimate tensile stress (UTS) of the monofilament is calculated according to the following equation:

$$\sigma_R = \frac{1}{3}\sum_{i=1}^{3}\sigma_i \qquad \text{with } \sigma_i = F/S_i \tag{1}$$

where F is the maximum load recorded during the test and S_i one of the three cross-section areas measured by laser diffraction.

The Young's modulus of the monofilament is calculated according to the following equation [27, 16]:

$$E = \frac{4}{\pi}\left[\frac{1}{3}\sum_{i=1}^{3}\left(\frac{L}{d_i^2}\right)\right]\frac{1}{C_a - C_s} \tag{2}$$

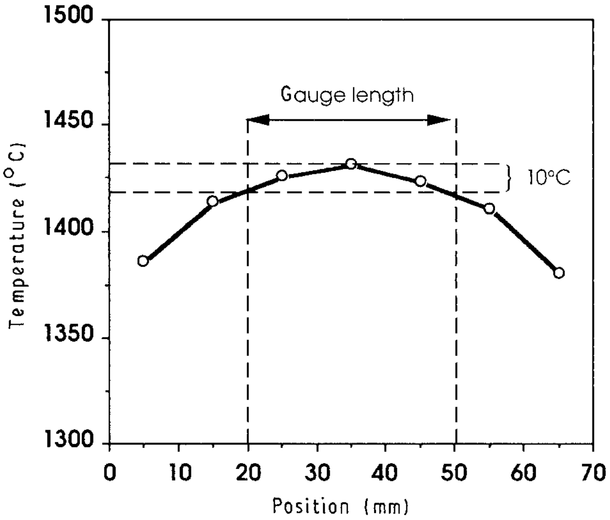

Figure 3 Temperature axial profiling of the hot zone of the tensile apparatus furnace (atmosphere: vacuum).

where C_a, the apparent compliance, is defined as

$$C_a = \Delta L/F \tag{3}$$

in which L is the gauge length, d_i the monofilament diameter and C_s the system compliance. The system compliance, i.e. the displacement per load unit resulting from all parameters or phenomena unrelated to the fibre material itself (e.g. the load cell, the two "grips", the MgO-based cement, the cement–fibre and cement–alumina tube joints, etc.) is obtained by extrapolating the curve corresponding to

$$C_a = f\left[\frac{1}{3}\sum_{i=1}^{3}\left(\frac{L}{d_i^2}\right)\right] \tag{4}$$

to $L/d^2 = 0$ (i.e. to a gauge length equal to zero), for each material and each test temperature.

Finally, the strain at failure, ε_R, is calculated according to

$$\varepsilon_R = \frac{\sigma_R}{E} \tag{5}$$

3. Results

3.1. Failure strength and Young's modulus at room temperature

The room-temperature UTS of both fibres was measured, with the same apparatus (but with different fibre–load cell and fibre–displacement table attachments on specimens taken from the same bobbin (ex-PCS Si–C–O fibre) or the same pyrolysis batch (ex-PCSZ Si–C–N(O) experimental monofilament). The data, as well as a probabilistic/deterministic model which can be used to predict the failure strength distribution at different gauge lengths from the experimental data measured at a given gauge length, have been presented in detail elsewhere [4, 28].

The mean UTS values (i.e. corresponding to a probability of failure of 0.5) for both fibres, at room temperature and for a gauge length of the order of 30 mm (i.e. that selected for the high-temperature tensile tests) have been calculated on the basis of the failure probability graphs shown in Fig. 4. For the ex-PCS Si–C–O fibre, the UTS is derived from a calculated curve (established itself from the experimental data obtained for $L = 50$ mm) whereas for the es-PCSZ Si–C–N(O), it is directly calculated from experimental data. The values are equal to 2370 MPa (Si–C–O fibre) and 1400 MPa (Si–C–N(O) fibre). The low value observed for the ex-PCSZ Si–C–N(O) fibre is thought to be related to the fact that: (i) it is a non-optimized experimental material and (ii) the specimens which have been used in the present work were from the tail of a batch (as a matter of fact higher mean UTS values, i.e. ≈ 2500 MPa, have been reported by Mocaer *et al.* [25] for specimens from the same batch).

The mean values of the Young's modulus at room temperature were observed to be 230 GPa for the ex-PCS Si–C–O fibres and 229 GPa for the ex-PCSZ Si–C–N(O) filament.

3.2. System compliances at high temperatures

The variations of the apparent compliance C_a (calculated according to Equation 3) as a function of the ratio L/d^2 (i.e. for specimens of different gauge lengths) are shown in Figs 5 and 6 for the two materials and for all the test temperatures. The system compliance C_s corresponds to the intersection of the $C_a = f(L/d^2)$ straight line with the ordinate axis, as already discussed in section 2.3. Its value was observed to be 112 μm N^{-1} for the ex-PCSZ Si–C–N(O) filament at 1200 °C and to range from 269 to 182 μm N^{-1} for the ex-PCS Si–C–O fibre as the test temperature is raised from 600 to 1400 °C.

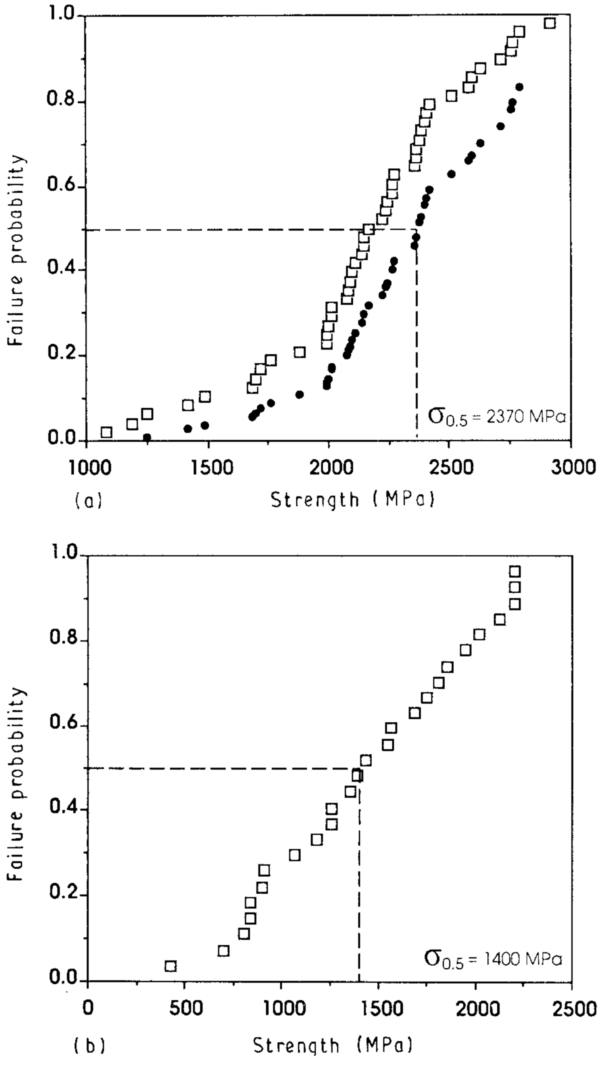

Figure 4 Room-temperature failure probability graphs for (a) ex-PCS Si–C–O fibre, (□) as measured for $L = 50$ mm and (●) as predicted according to a probabilistic/deterministic model for $L = 30$ mm [28], and (b) ex-PCSZ Si–C–N–(O) fibre, as measured for $L = 25$ mm.

3.3. High-temperature tensile test data

The variations of both the mean UTS and Young's modulus of the ex-PCS Si–C–O fibres, tested under vacuum in present work, are shown in Fig. 7. As expected from previous work on ceramic fibres, the fibre strength is observed to decrease dramatically when the test temperature is raised from room temperature to 1400 °C (the decrease in strength being already significant at 800 °C). Furthermore and generally speaking, the strength loss appears to be more pronounced for tests performed in a vacuum (present work) than for tests performed in air (Pysher *et al.* data [14]), as expected from the metastable character of this fibre. This feature will be discussed in a more detailed manner in the next section. Conversely, the temperature dependence of the Young's modulus as established in the present work (Fig. 7b) is much less pronounced, a feature which is not in agreement with the data previously reported by Pysher *et al.* for tests performed under different experimental conditions [14].

The strength and stiffness retentions at 1200 °C of the ex-PCSZ Si–C–N(O) experimental monofilament, as measured in tests performed either under vacuum (residual pressure less than 0.1 Pa) or in nitrogen ($P = 100$ kPa), are shown in Fig. 8. It appears that the temperature effect observed in the tests performed under vacuum is similar to that reported above for the ex-PCS Si–C–O fibre namely: (i) an important decrease of the failure strength (which is even more pronounced for the nitrogen-containing material) and (ii) almost no change in Young's modulus. Furthermore, the nature of the test atmosphere has a dramatic effect on the strength retention at high temperatures: when tested at 1200 °C under vacuum, the fibre is observed to have lost 80% of its room-temperature strength whereas in an atmosphere of nitrogen ($P = 100$ kPa) no strength loss occurs any longer (the strength of the fibre being even slightly higher at 1200 °C than at 25 °C). Obviously such a feature has to be explained on the basis of the decomposition process of the material which has been described by Mocaer *et al.* [24, 25]. This point will be further discussed in the next section.

Since no polymeric coating could be applied to the specimen in order to avoid the effect of the shock wave generated in the material when failure occurs [4], it was not usually possible to recover the specimen fragment corresponding to the actual failure for a scanning electron microscope analysis of the failure surface and critical defect identification.

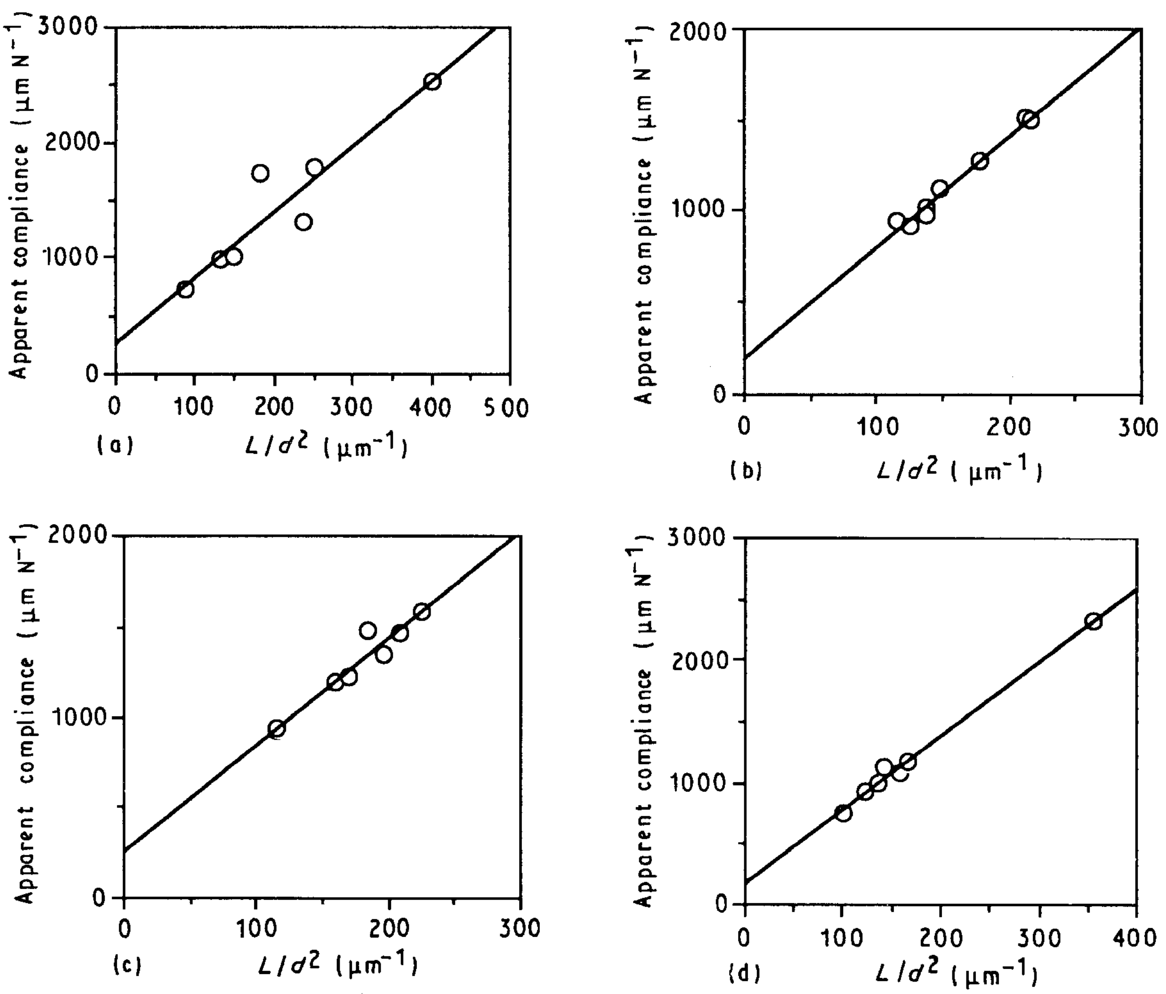

Figure 5 Apparent compliances of ex-PCS Si–C–O fibres under vacuum at (a) 600 °C, (b) 800 °C, (c) 1100 °C, (d) 1400 °C leading to system compliances of 269, 194, 254 and 182 µm N^{-1}, respectively.

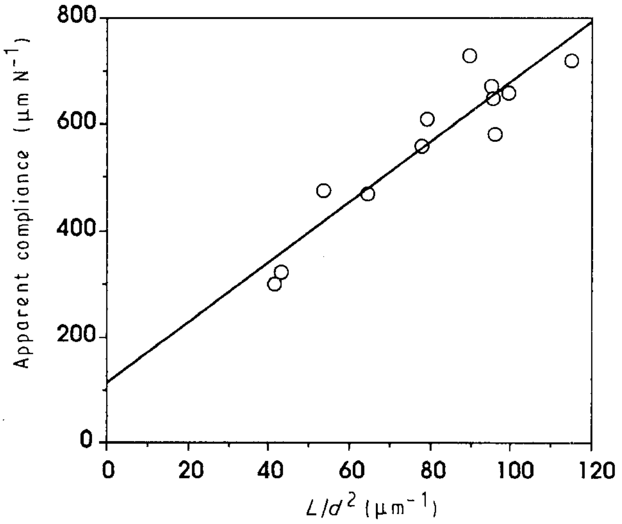

Figure 6 Apparent compliance of Si–C–N–(O) fibres at 1200 °C under vacuum or nitrogen, leading to a system compliance of 112 µm N^{-1}.

4. Discussion

4.1. System compliance

The actual value of the system compliance C_s results from different contributions, some of them depending on the test temperature. This is particularly the case for the joints between the fibre specimen and the alumina tubes since these joints, in the experimental procedure which has been selected in present work, are exposed to the test temperature. Thus, some variations of the joint compliance are expected as the test temperature is increased related to: (i) a possible change in the stiffness of the MgO-based cement, (ii) a clamping effect resulting from differential thermal expansion between the filament, the cement and the alumina tubes, and eventually (iii) chemical reaction which might occur between the filament and the cement at high temperatures. For all these reasons it was thought that the only appropriate way to make a reliable compliance correction was indeed to calculate the system compliance C_s at each test temperature and for each filament.

For the ex-PCS Si–C–O fibre, the system compliance is observed to decrease from 269 to 182 µm N^{-1} as the test temperature is raised from 600 to 1400 °C. This change is thought to be related mainly to an increase of the radial thermal stress resulting from the difference in the CTEs of the MgO-based cement ($\alpha = 12.6 \times 10^{-6}\,°C^{-1}$), on the one hand, and the alumina tubes ($\alpha = 8.1 \times 10^{-6}\,°C^{-1}$), on the other hand. As the test temperature is raised, the resulting clamping effect becomes higher and higher and thus the sliding of the fibre within the cement is more and more difficult. As a matter of fact, it has been observed that at 600 °C, sliding almost always occurs

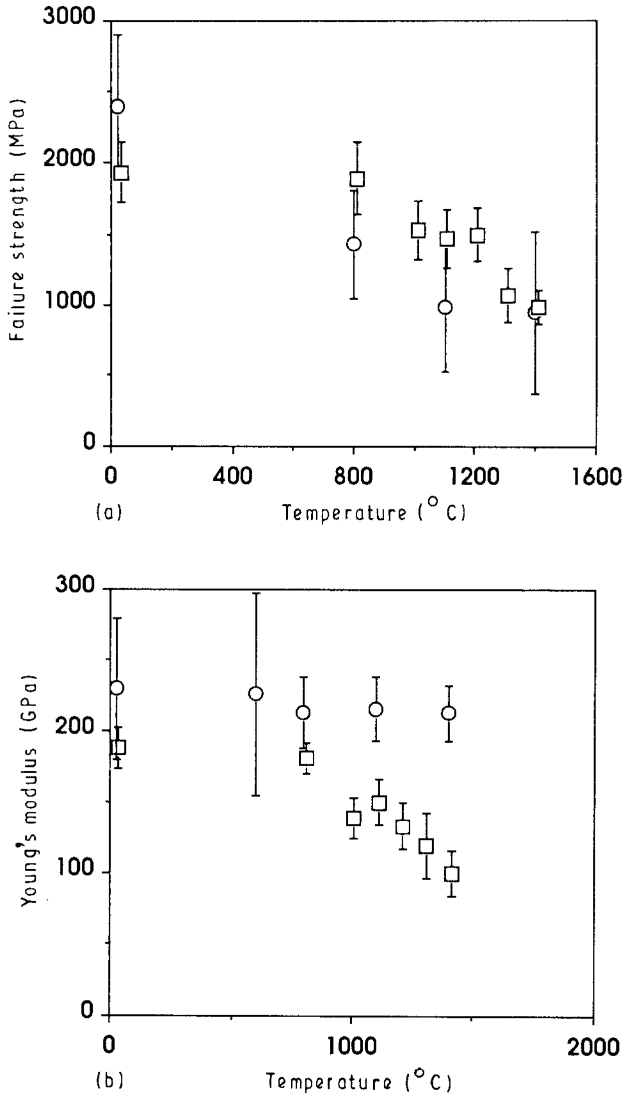

Figure 7 Variations of the mechanical tensile properties of ex-PCS Si–C–O fibres as a function of the test temperature: (a) failure strength and (b) Young's modulus. The data from the present work (○) were obtained under vacuum whereas those reported by Pysher *et al.* [14] (□) were recorded in air. The errors bars in (a) represent respectively 95% (Pysher *et al.*) and 68% (present work) confidence limits and those in (b) 95% confidence limits for both sets of data.

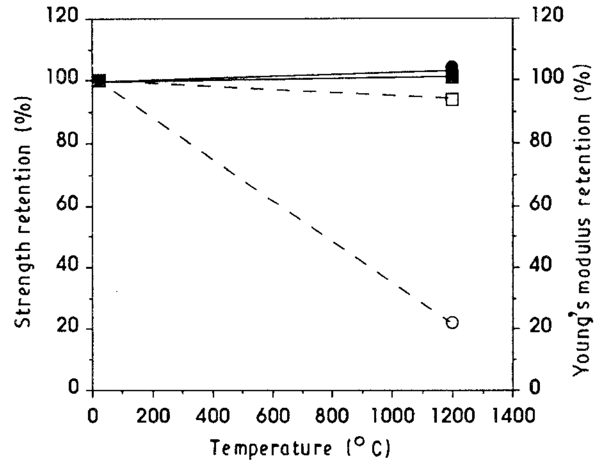

Figure 8 Properties at 1200 °C of Si–C–N(O) fibre under vacuum (0.1 Pa) and in nitrogen (100 kPa). Under vacuum: (○) strength, (□) modulus. In nitrogen: (●) strength, (■) modulus.

at a high enough applied load. Therefore and as shown in Figs 5 and 7, the data recorded at this low temperature were used to derive the Young's modulus (at low applied loads) but were not taken into account for the calculation of the failure strength. Finally, the system compliance determination, according to the procedure described in section 2.3, was observed to be much more accurate [16] when one or several tests were performed with a gauge length higher or lower than 30 mm. As an example, in Fig. 5d the majority of the data points correspond to a gauge length close to 30 mm (for $L = 30$ mm and $d = 15$ μm, the value of the ratio L/d^2 is 133 μm^{-1}) with the exception of the data point at $L/d^2 \approx 360$ μm^{-1} corresponding to $L = 43.5$ mm and $d = 11.1$ μm. Conversely, the failure strength which could be calculated for this gauge length (very different from the nominal gauge length of 30 mm) was not taken into account in the calculation of the mean UTS value, since it is well known that the failure strength of a ceramic fibre depends strongly on the gauge length.

For the ex-PCSZ Si–C–N(O) experimental filament, the value of the system compliance derived from the experiments performed at 1200 °C (Fig. 6) is still lower than the lowest value observed for the related ex-PCS Si–C–O fibre. This result could be explained by the fact that the Si–C–N(O) filament has a mean diameter, i.e. 16.8 μm, significantly higher than that of the Si–C–O fibre (which is only 14.3 μm). Thus, the circumferential surface area available for the fibre–cement joint is higher for the former than for the latter (the ratio of the joint surfaces, for a given joint length, being about 1.4).

Finally, one could argue about the occurrence of chemical reactions at high temperatures between the MgO-based cement and the Si–C–O and Si–C–N(O) filaments, which could change the chemical bonding and locally weaken the material. Generally speaking, MgO is known as a very stable oxide. Furthermore, if one assumes that the external surface of the specimens consists of a thin layer of silica, a chemical reaction between MgO and SiO_2 might well occur yielding a magnesium silicate which could strengthen the chemical bonding between the cement and the ceramic filament. However, it was assumed that such a chemical reaction was not detrimental to the specimen failure strength owing to the short time during which that chemical reaction can take place (with a heating rate of 100 °C min^{-1}, the joints are exposed to temperatures higher than 1000 °C during 3–5 min only for test temperatures ranging from 1200 to 1400 °C).

4.2. Variations of the failure strength and Young's modulus with test temperature

4.2.1. Si–C–O fibre

As shown in Fig. 7a, the failure strength of the ex-PCS Si–C–O fibre is observed to decrease significantly (i.e. from ≈2350 to ≈900 MPa) as the test temperature is raised from 25 to 1400 °C, for experiments performed under vacuum (the residual pressure in the test chamber being of the order of 0.1 Pa). These results are in good agreement with the high-temperature data recently reported by Pysher *et al.* [14] for the same material but for tests performed in air. In both cases, the strength retention at 1400 °C is of the order of 40% with respect to the failure strength at room temperature.

In an early study, Simon [15] and Bunsell and Simon [13] have reported similar failure strength drops at 1400 °C for related materials, namely: (i) strength retentions of 44 and 23% for NLP 101 grade fibre tested in argon and air, respectively, and (ii) a strength retention of 54% for NLM 102 fibre tested in air (both Nicalon fibres (standard grade) from Nippon Carbon). Finally, a number of authors have reported a significant decrease in strength at room temperature after ageing treatments performed on ex-PCS Si–C–O fibres at high temperatures and under a variety of atmospheres. As an example, Jaskowiak and Di Carlo [10] have mentioned strength retention values of 54% and 17% after an ageing treatment of 1 h performed under vacuum at 1100 and 1400 °C, respectively. The high-temperature failure strength data from the present work are thus consistent with those previously reported for the same (or related) materials.

Conversely, our high-temperature Young's modulus data for the ex-PCS Si–C–O fibres are somewhat different from those previously published by Simon [15] or Pysher *et al.* [14]. As shown in Fig. 7b, the decrease in stiffness experienced by the fibre when the test temperature is raised from 25 to 1400 °C is very limited, the stiffness retention at 1400 °C being of the order of 90%. This high retention value contrasts with those obtained by Pysher *et al.*, i.e. 54% for tests performed in air on the same material, or by Simon, i.e. 55 and 43% for tests performed in air and argon, respectively, on older ex-PCS Si–C–O fibres.

4.2.2. Si–C–N(O) fibre

As shown in Fig. 8, the failure strength decrease observed for the ex-PCSZ Si–C–N(O) fibre under vacuum, when the test temperature is raised from 25 to 1200 °C (i.e. up to the temperature at which the fibre has been processed), is still more significant than that reported above for the ex-PCS Si–C–O material. At 1200 °C, the strength retention is only 20% (versus ≈40% for the Si–C–O fibre). Furthermore, it is found to be strongly dependent on the nature of the test atmosphere. As a matter of fact, there is no longer any strength loss, even at a temperature as high as 1200 °C, when the tensile test is performed in pure nitrogen ($P = 100$ kPa). This result is consistent with those reported very recently by Mocaer *et al.* [25] for failure strength measurements performed at room temperature as a function of the processing temperature θ_P (pyrolysis in an atmosphere of pure nitrogen), on specimens taken from the same batch as those tested in present work: when θ_P was raised from 1200 to 1400 °C, the failure strength at 25 °C falls by only 10%.

The effect of the test temperature on the Young's modulus is low: a slight decrease is observed for tests performed under vacuum whereas the Young's modulus slightly increases at 1200 °C when the tests are performed in nitrogen. It is worthy of note that Mocaer *et al.* [25] reported that the Young's modulus of the ex-PCSZ Si–C–N(O) filament measured at 25 °C increases slightly when the processing temperature θ_P (pyrolysis step in nitrogen) was raised from 1200 to 1600 °C.

4.2.3. Thermal stability of fibres

The variations of the mechanical properties of the ex-organosilicon Si–C–O and Si–C–N(O) ceramic fibres as a function of the test temperature, as observed in the present work, can be explained (at least in their main trends) on the basis of the thermal stability of the fibres as already suggested to explain the effect of ageing treatments on their room-temperature characteristics [3, 7–11, 23–25].

Generally speaking, these fibres (either purely amorphous or poorly crystalline) are in a metastable state at high temperatures. When their temperature is raised at a high enough value (which depends on their chemical composition), a decomposition process occurs with: (i) an evolution of gaseous species, namely SiO and CO for the Si–C–O fibres prepared from oxygen-cured PCS-precursors [2, 3] or nitrogen for the Si–C–N fibres [25] obtained from γ-ray-cured PCSZ precursors and almost oxygen-free (and even gaseous silicon in both cases if the temperature is very high), and simultaneously (ii) the formation of a porous pyrolytic solid residue which undergoes a crystallization process and exhibits weak mechanical characteristics. This decomposition process is thought to start at the surface of the filament and to move radially towards its axis with kinetics depending on both temperature and test atmosphere, as shown schematically in Fig. 9. These kinetics are accelerated when the temperature is raised and/or the treatment is performed under vacuum. Conversely, they are slowed down when it is performed under an external pressure of one of the gaseous species involved in the decomposition process, e.g. CO for the Si–C–O fibres [29] or nitrogen for the Si–C–N(O) experimental monofilaments [25].

The formation of a porous layer of pyrolytic residue (even of low thickness) at the filament surface introduces a new population of surface flaws whose sizes rapidly become larger than those of the initial defects of the fibre, yielding thus a decrease in the failure strength (Fig. 9b). As the thickness of the decomposed zone increases (Fig. 9c), the Young's modulus of the composite fibre (which consists to a first approximation of an unchanged stiff core surrounded by a porous shell of low stiffness) decreases. Finally, for very severe treatments the whole initial fibre can be totally decomposed (Fig. 9d).

The high-temperature data obtained in the present work for the ex-PCS Si–C–O fibres which are shown in Fig. 7 suggest that the decomposition process, known to start at about 1100 °C in argon or in air (and which could be effective at lower temperatures under high vacuum), could have been limited to the stage schematically shown in Fig. 9b as supported by (i) the

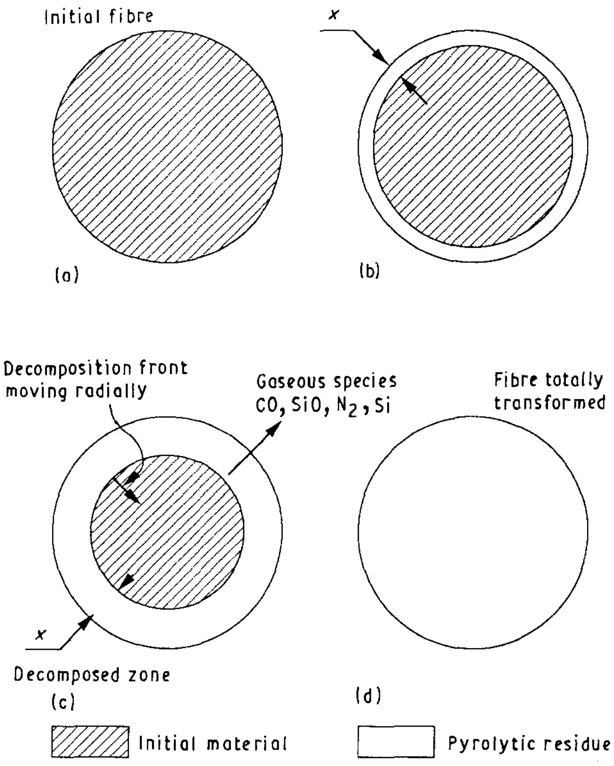

Figure 9 Successive stages (schematic) in the decomposition process of an ex-organosilicon ceramic fibre: (a) initial homogeneous fibre with intrinsic volume/surface flaws, (b) early decomposition stage (the flaws of the pyrolytic layer rapidly control the filament failure even when x is small but the effect on the modulus is low), (c) intermediate stage (when x is large enough the modulus, given by the rule of mixtures, decreases significantly) and (d) final stage (the decomposition front has reached the filament axis).

decrease in failure strength and (ii) the low change in Young's modulus. Furthermore, the fact that the present σ_R data points (corresponding to tests performed under high vacuum) lie almost systematically well below those reported by Pysher *et al.* for tests performed in air and with longer exposure to high temperatures [14] is consistent with what has been said above on the kinetics of the decomposition process. Additionally, the absence of any significant decrease in the Young's modulus with respect to the data of Pysher *et al.* could be related to the rapidity of the high-temperature excursion undergone by the specimens in the present work (e.g. 3 and 5 min beyond 1000 °C for tests run at 1200 and 1400 °C, respectively). Under such conditions, it is thought that the decomposition is significant enough to yield a new population of surface flaws large enough to reduce σ_R but too limited to markedly affect the Young's modulus.

The high-temperature data shown in Fig. 8 for the ex-PCSZ Si–C–N(O) experimental filament are also consistent with the qualitative thermal decomposition model depicted above. When tested under high vacuum, the results (although more limited in volume) are similar to those reported for the Si–C–O fibre. The decomposition process, which is known to yield mainly an evolution of nitrogen beyond about 1400 °C in argon ($P = 100$ kPa) according to Mocaer *et al.* [24, 25], is shifted at lower temperatures (i.e. 1200 °C) and accelerated by the vacuum. It results in a strength decrease with almost no change in the Young's modulus (suggesting again that the decomposition is limited to the stage shown in Fig. 9b). Conversely, when the tests are performed in nitrogen ($P = 100$ kPa), no decomposition occurs at 1200 °C with the result that both the failure strength and Young's modulus remain unchanged. This absence of any decomposition of the Si–C–N(O) filament under a pressure of 100 kPa of nitrogen has been already established by Mocaer *et al.* from ageing experiments and reported to remain hardly detectable up to 1400–1600 °C [25].

5. Conclusion

A simple micro-tensile tester has been designed and used to characterize two ex-organosilicon ceramic fibres at high temperatures with the following main conclusions.

1. The choice of an induction-heated furnace enables fast heating rates and high test temperatures to be used, with the result that the specimen experiences only a short excursion (i.e. a few minutes) in the temperature range of interest (from 1000 to 1600 °C for ex-organosilicon fibres). Under such conditions, the effect of creep occurring in the material during the test is limited.
2. The tensile tests can be performed either under vacuum (residual pressure 0.1 Pa) or in controlled atmospheres including gaseous species which might play a role in the equilibrium state of the fibres at high temperatures (e.g. nitrogen or carbon monoxide).
3. The choice of a rather short gauge length (i.e. 30 mm) entirely set in the isothermal zone of the furnace, and the use of a system compliance correction, permits measurements of the Young's modulus at high homogeneous temperatures. Conversely, this choice implies small displacements and hot grips. A high-temperature MgO-based cement was used to mount the specimen on alumina tube holders.
4. The ex-PCS Si–C–O fiber was observed to undergo an important strength loss when tested in the 1000–1400 °C range, under vacuum. This loss, already reported for tests performed in argon or in air, is assigned to a decomposition process with an evolution of gaseous species (CO and/or SiO) and which is thus accelerated by the vacuum. Conversely, no significant decrease in the Young's modulus was observed, possibly due to the short duration of the exposure to high temperatures.
5. The ex-PCSZ Si–C–N(O) experimental filament behaves in a similar way. A still more significant strength drop is observed under vacuum, assigned to a decomposition process with an evolution of nitrogen. Conversely, no decomposition and hence no strength loss occur when the test is performed in an atmosphere of nitrogen ($P = 100$ kPa) at 1200 °C. Finally, under both test conditions, the Young's modulus remains unchanged when the temperature is raised from 25 to 1200 °C.

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