JOURNAL OF MATERIALS SCIENCE 30 (1995) 5813–5818

Tensile strength of silicon carbide fibre bundles at elevated temperatures

G. EMIG
Institut für Technische Chemie I, Universität Erlangen, Egerlandstraße 3, D-91058 Erlangen, Germany

R. WIRTH
Institut für Chemische Technik, Universität Karlsruhe, Kaiserstraße 12, D-76128 Karlsruhe, Germany

The mechanical properties of commercially available SiC-based ceramic fibres were measured in the temperature range from 400–1300 °C. The measurements were performed in air and in inert gas atmospheres, respectively. The Nicalon™ and Tyranno™ fibres were tested as filament bundles and the decrease in strength occurring at temperatures above 600 °C was found in both atmospheres. To obtain a well-defined gauge length at the testing temperature, a furnace with very steep temperature gradients at both ends was built. To eliminate grip-induced damage in the heating zone the fibre bundles were fixed outside the furnace with cold grip units. These grips guaranteed the uniformity of load distribution imposed on to each of the individual filaments in the fibre bundle. A significant shrinkage of the fibres occurring during the creep test performed under low loads indicates a change in the microstructure of the fibres at high temperatures.

1. Introduction

The high-temperature behaviour of advanced ceramic matrix composites (CMCs) strongly depends on the thermomechanical stability of the reinforcing ceramic fibres. The compatibility of the fibre matrix is also a major factor to be considered but the ultimate limits for such composite systems depend on the stability of the ceramic fibre. Here the properties of reinforcing fibres in relation to oxidation, creep and stress rupture as a function of temperature, applied stress and environment are the most interesting problems.

Several studies of room-temperature mechanical properties after high-temperature exposure of silicon carbide fibres in different environments have been reported [1–4]. So far, only silicon carbide monofilaments were tested. The results lead to the conclusion that fibres are inherently unstable when heat treated above their processing temperature of 1200 °C.

Investigations on the creep behaviour and time-dependent strength (stress rupture) of monofilaments at temperatures up to 1300 °C have also been published previously [5–7]. The determination of high-temperature properties of ceramic fibres by studies of single filaments only leads to results that may not be representative for the whole fibre bundle. Therefore, a new method for testing multifilament yarns was used in the present study. Two types of commercially available silicon carbide fibre bundles (Nicalon™ NLM102 and Tyranno™ TY-S1H08PX) were tested.

The objective of these studies was to establish a testing method for the creep behaviour of ceramic fibre bundles at temperatures up to 1300 °C in oxidizing or inert gas atmospheres.

2. Experimental procedure

The fibres were received as filament bundles consisting of approximately 800 (Tyranno™) and 500 (Nicalon™) filaments, respectively.

Prior to measurement of the mechanical properties of the fibres, the sizing agent was removed by extraction with methylethylketone in a Soxlet apparatus for several hours. Then the fibre bundles were dried at 120 °C for 2 days.

2.1. Testing apparatus

To perform detailed measurements of mechanical properties of fibre bundles one major problem has to be solved. This is the uniformity of load distribution imposed on each of the individual filaments in a fibre bundle. A special apparatus for the suspension of the bundles in the testing machine was used, as shown schematically in Fig. 1. Three loops of fibre bundles were wound around two cylinders (diameter 60 mm) and straightened by the machine while adjusting the primary load of 10 N. The friction between the fibres and the polished surface of the cylinders was used to fix the bundles during the measurement. The primary fixation unit in Fig. 1 was only used for preparing the measurement.

With this equipment, stress–strain diagrams, as shown in Fig. 2, were obtained. A straight line is

0022–2461

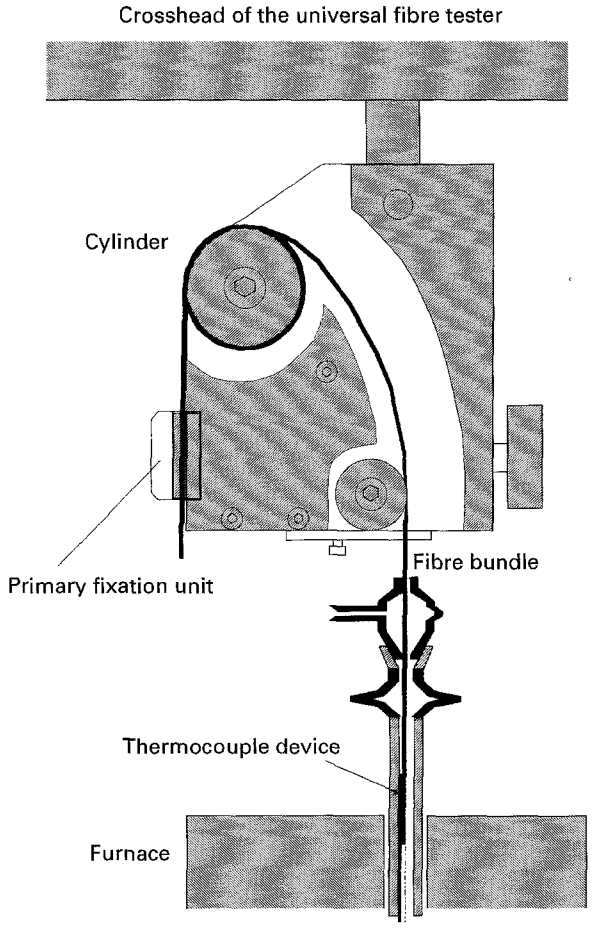

Figure 1 Cable winding unit.

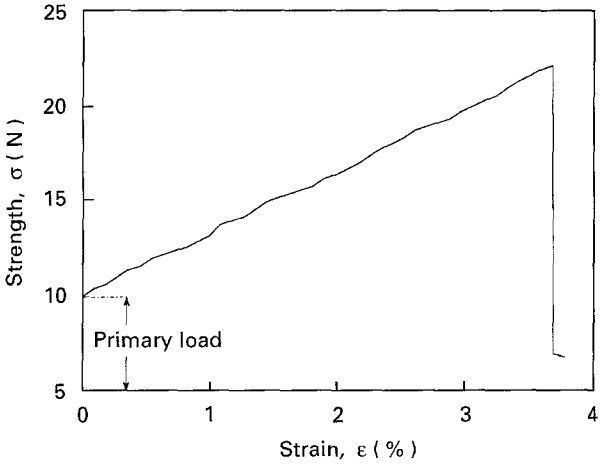

Figure 2 Stress-strain diagram.

observed, followed by catastrophic failure as expected for materials following Hooke's law. This is typical for refractory materials showing the uniformity of the distribution of the load on to the individual monofilaments.

Four lamps (output 4 kW) were used to heat the furnace. The light was reflected by mirrors leading to a uniform distribution of the heat. The furnace is shown schematically in Fig. 3. This arrangement leads to a uniform temperature in the furnace with a very steep temperature gradient at both ends. The temperature profile of the furnace was measured quite accurately for temperatures ranging from 400–1300 °C. The results are shown in Fig. 4.

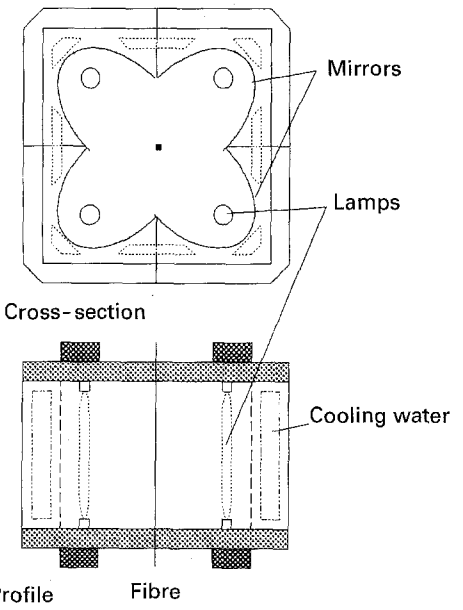

Figure 3 The furnace unit.

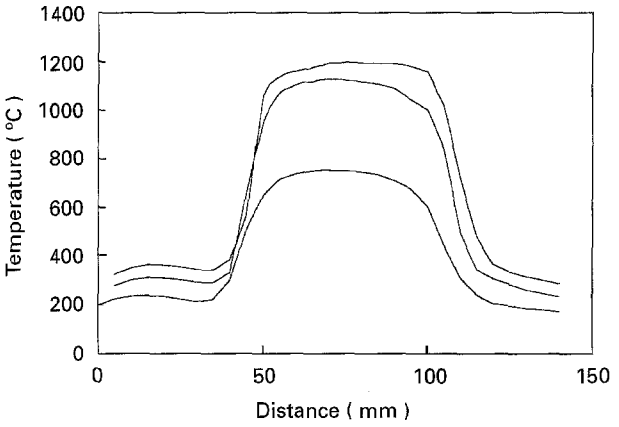

Figure 4 Heating zone profile of the furnace.

Obviously, the length of the isothermal zone does not vary significantly if the temperature is varied by 100 °C, so that a linear interpolation is justified. Therefore, it is possible to define a well-known gauge length especially for the creep tests [6, 11]. Inside the furnace the fibres were fed through a quartz tube that could be filled with air or inert gas. For the evaluation, only experiments in which failure was within the isothermal zone were considered. Failure due to thermal stresses induced by the temperature gradient at the ends of the furnace was thereby excluded. During the tests the temperature was monitored using a blackened Pt/RhPt thermocouple placed parallel to the fibre bundle in the middle of the isothermal zone of the furnace.

Only long specimens could be tested due to the size of the furnace. The gauge length between the grips was 350 mm, the effective gauge length subjected to the test temperature was approximately given by the length of the heating zone of the furnace.

The testing equipment was a computer-controlled testing machine (UTS Company, UTS10), the chuck (cable winding unit) was also built by UTS, the furnace was built with assistance from the Institut für Werkstoffkunde I of the University of Karlsruhe.

2.2. Testing methods

Tensile strength tests and creep rupture tests on the fibre bundles were both conducted in argon and air, respectively; the total pressure was 1 bar. The tensile strength tests were performed at temperatures ranging from 400–1300 °C. First, the fibre bundles were fixed in the testing machine. The gas inlets were opened and the thermocouple device was positioned parallel to the fibre bundle. To exclude any oxygen in the atmosphere during the tests in argon, the apparatus was evacuated and then filled with dry argon several times. The furnace was heated to testing temperature at approximately 100 K min^{-1}. The bundles were held at the testing temperature for 1 min to ensure that the final temperature was reached and that the axial temperature distribution was uniform. Then the testing machine was started using a crosshead speed of 20 mm min^{-1} until the fibre bundles were stretched (primary load of 10 N). During the measurement of the ultimate tensile strength the length of the fibres was determined from the position of the crosshead. The speed of the crosshead was kept constant (10 mm min^{-1}) and the resulting force was measured by a load cell.

For the creep tests, a load corresponding to approximately 5%, 10% and 15% of the load of failure at the testing temperature was imposed on to the bundle. Subsequently, the testing temperature was adjusted using a heating rate of 100 K min^{-1}.

3. Results

3.1. Tensile tests at elevated temperatures

The tensile strength of Nicalon™ and Tyranno™ fibres was measured as a function of testing temperature in two different atmospheres. The results are shown in Figs 5–7. Each point represents the average of at least ten tests. Error bars represent 95% confidence limits. In Fig. 5 the results of the measurements of the tensile strength of Nicalon fibres performed in air and in an argon atmosphere are shown. One can recognize that in both atmospheres the tensile strength is nearly constant for temperatures up to 400 °C. In the case of the measurements performed in air, the tensile strength increased by about 10% in the temperature range from 400–450 °C. This effect can be explained by partial filling of surface defects with silica [12]. For higher testing temperatures, the tensile strength of the Nicalon fibres decreases considerably, levelling out at about 25% of the maximum value. In the case of the measurements performed in an argon atmosphere, however, the tensile strength is constant up to about 550 °C. In the temperature range from 550–1000 °C, an almost linear decrease of the tensile strength with increasing temperature was observed. At higher temperatures the tensile strength decreases considerably and at a testing temperature of 1300 °C the strength of the fibre was practically at the same level as that observed in air.

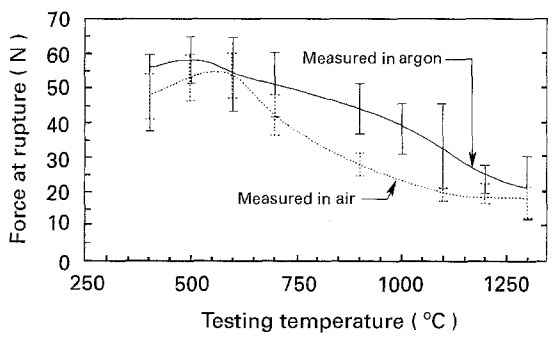

Figure 5 Nicalon fibre bundles.

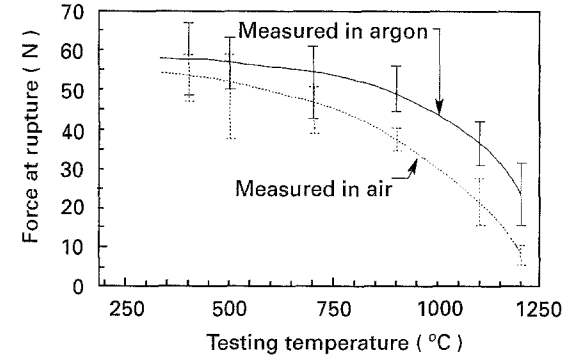

Figure 6 Tyranno fibre bundles.

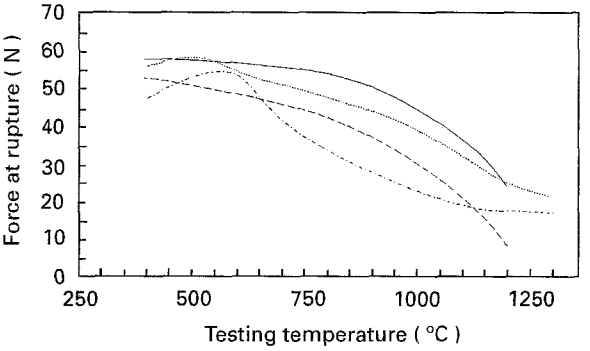

Figure 7 Comparison between (···, – – –) Nicalon and (—, – – –) Tyranno fibre bundles, measured in (—, ···) argon, and (– – –, — · —) air.

The decrease of the tensile strength of the Nicalon fibres occurring at relatively low temperatures can be explained by reactions between different components of the fibres (when heated in argon) and of reactions between the fibres and the gas phase (when heated in air). During rapid densification of the fibres in the pyrolysis step, the fibres degas through surface-connected porosity. After pyrolysis is complete, further heating apparently collapses these channels to globular pores. As a result of these nanopores the fibres undergo irreversible morphological changes on heating which cause the formation and growth of flaws, thus reducing the filament strength. The decrease of the tensile strength observed during the measurements performed in an argon atmosphere at higher temperatures can be explained by the weakening of the fibres by chemical reactions within the fibre bulk [13, 14] indicating the thermodynamic instability of the composition.

The removal of the sizing agent by solvent extraction leads to a carbon-rich near-surface region of the fibre bundles [14]. The reactions between the excess

carbon and the oxygen bonded to silicon leading to the formation of CO strongly increases at temperatures of about 1000 °C [1, 15, 16] which explains the strong decrease of the tensile strength at testing temperatures above 1000 °C. The weakening of the fibres at higher temperatures was associated with CO evolution and SiC grain growth. These degradation reactions are irreversible and diffusion rate-limited in an inert atmosphere [17].

The measurements performed in air, however, indicated that here the fibres are predominantly damaged by the oxidation of the excess carbon in the near-surface region. The strong exponential dependence of the reaction rate constant on the temperature leads to a very fast development of the volatile products (CO) leaving pores at the former sites of the excess carbon. As a result, the fibres are weakened. In contrast to the measurements performed in argon, the amount of weakening was reduced as the air-measurement temperature increased. This was attributed to the formation of a protective silica layer, which limits the diffusion rate of the product gases through the surrounding boundary layer out of the fibre. The solid-state reactions between excess carbon- and oxygen-containing silicon compounds are of minor importance, indicated by the almost constant tensile strength of the Nicalon fibres observed at testing temperatures above 1000 °C.

In Fig. 6 the results of corresponding measurements of the tensile strength of the Tyranno fibres are shown. One can recognize that for the Tyranno fibres, the force at failure is at the same level as that measured in the Nicalon fibres. With increasing testing temperature the tensile strength of the fibres decreases and the slope of the curves shown in Fig. 6 increases with increasing testing temperature. As a contrast to the results observed in the case of Nicalon fibres, there is no maximum of the tensile strength at high temperatures as shown in Fig. 7 [18]. This effect could be a result of a possible post-pyrolysis heat-treating step in air at UBE Industries or is more likely attributed to the higher amount of oxygen in the Tyranno fibre (see Table I). The loss of strength at lower temperatures is smaller than for the Nicalon fibres. The Tyranno fibre composition shows a predominantly amorphous phase consisting of Si–C–O–Ti. This composition has a reduced tendency to crystallize at higher temperatures compared to the Nicalon fibres [14]. The rapid decrease of the tensile strength observed at testing temperatures above 600 °C in air and 800 °C in argon atmosphere, respectively, can be explained by thermal decomposition of the oxygen-rich Tyranno fibre. In comparison with Nicalon fibres, the total loss of strength with no final value can be explained by the higher oxygen content and with the smaller diameter of the fibres leading to a negligible cross-section after pore formation arising from the volatile products.

3.2. Creep tests

As described in Section 2.2, the creep behaviour of both fibre types was measured at different temperatures in argon and in air (flow rates in both cases approximately 200 ml min^{-1}), respectively. The elongation was measured as a function of the time. A typical curve is shown in Fig. 8. Using the slope of the curve obtained during heating, the coefficient of thermal expansion (CTE) was calculated by linear regression. The CTE was determined to be $2.4–2.8 \times 10^{-6} K^{-1}$ for the Tyranno fibre and $3.2–3.33 \times 10^{-6} K^{-1}$ for the Nicalon fibre. The good agreement with data reported in the literature ($3.1 \times 10^{-6} K^{-1}$ for both fibres) [19] leads to the conclusion that the length of the heating zone as shown in Fig. 4 is correct. The time at which the testing temperature was reached was identified with the value $t = 0$ in Figs 9–11.

In Fig. 9 the results of the creep measurements performed in argon atmosphere using a load of 5% of the load at failure are shown. At low temperatures, for the Nicalon fibre, a creep behaviour expected for steady-state creep was observed. Owing to crystallite growth and pore size decrease as reported elsewhere [9, 17], shrinkage is superposed on the creep curve at a testing temperature of 1200 °C. In the case of the Tyranno fibres, basically the same effects were observed. The temperature at which the shrinkage starts (1000 °C), however, is at least 100 °C lower than in the case of the Nicalon fibre (1100 °C). Free carbon was found to inhibit creep in ceramic fibres derived from polymer precursors [14]. The concentration of excess carbon in the Tyranno fibre at higher temperatures is lower than in the Nicalon fibre. The higher amount of

TABLE I Properties of the investigated fibres

Name and manufacturer	Composition (wt %) and phases [14]	Diameter (μm)	Number of fibres in bundle
Nicalon NLM102 Nippon Carbon Co.	56 Si, 30 C, 14 O [8, 9] Siliconoxycarbide (amorphous) dispersed excess carbon dispersed β-SiC (microcryst.) dispersed, closed nanopores	13	approx. 500
Tyranno TY-S1H08PX UBE Industries	45 Si, 25 C, 23 O, 3 Ti [10] Si–C–O–Ti phase (amorphous) dispersed excess carbon dispersed, closed nanopores small amounts of SiC and TiC	8.25	800

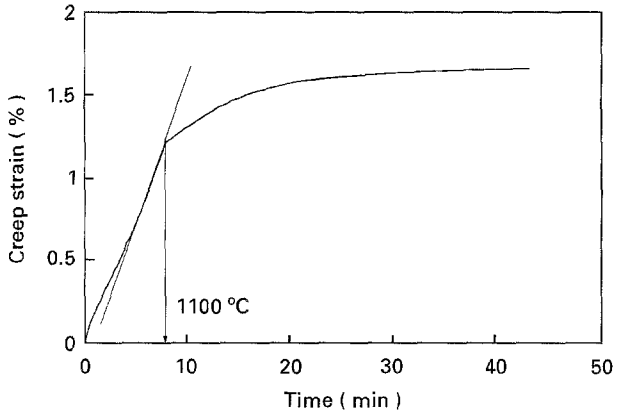

Figure 8 Coefficient of thermal expansion, of Nicalon fibre bundles, measured at 1100 °C in argon with an applied load of 5% of the force at rupture.

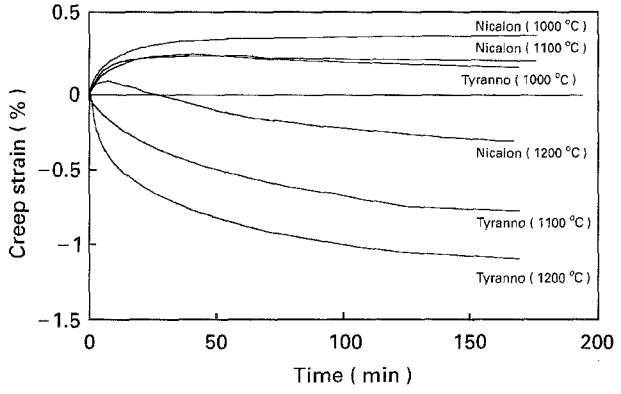

Figure 9 Creep behaviour of Nicalon and Tyranno fibre bundles measured at 1000, 1100 and 1200 °C, with an applied load of 5% of the force at rupture.

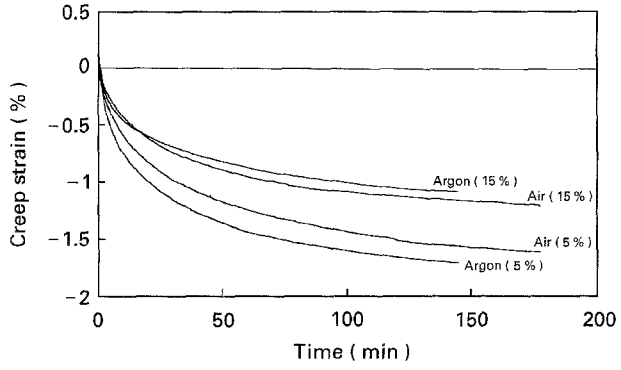

Figure 10 Creep strain as a function of time for different stresses, in Tyranno fibre bundles, at 1200 °C.

oxygen in the composition of Tyranno fibres leads to a much faster decomposition of the excess carbon at higher temperatures. Accordingly, at the high testing temperatures (1100 and 1200 °C) a strong shrinkage of the Tyranno fibre was observed. Owing to the strain-to-failure, cracks in the silica layer at the surface of the fibre can occur and thus the oxidation of excess carbon and the solid-state reactions can be accelerated.

In Fig. 10 the creep strain is shown as a function of time for different stresses. The figure shows the results from experiments performed in air and argon atmospheres for two different loads (5% and 15% of the load at failure). For the high load no significant influence of the gas atmosphere was observed, whereas in the case of the low load, the shrinkage in an argon atmosphere was significantly stronger than the shrinkage observed in air. This behaviour can be explained in terms of the effects of the mechanical stress and of the formation of a near-surface silica layer by oxidation. The silica formed by the oxidation of silicon compounds is known to decrease the amount of volatile CO produced from the excess carbon. The reduction of the concentration of free carbon in the fibres is pushed back and the creep rate is therefore decreased. By superposition of the creep under the influence of the mechanical stress and the shrinkage caused by solid-state reactions in the bulk of the fibre, the lower rate of the total strain can be explained. With increasing load the rate of creep caused by the mechanical stress is expected to increase.

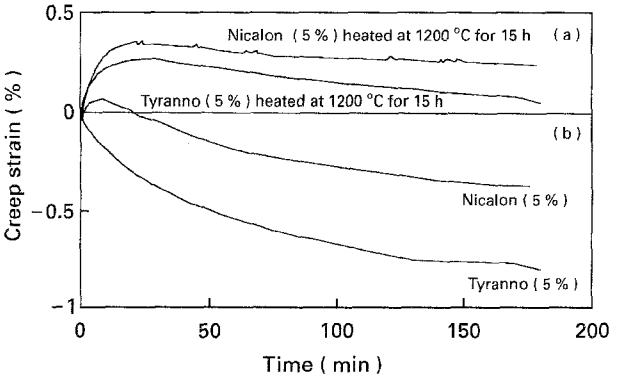

Figure 11 Creep behaviour of Tyranno and Nicalon fibre bundles (a) heated in argon at 1200 °C for 15 h, and (b) untreated. The Nicalon fibre bundles were measured at 1200 °C, the Tyranno fibre bundles were measured at 1100 °C.

3.3. Creep after heat treatment

As mentioned above, the results of the creep experiments indicate that the creep rate decreases and the length change levels out at constant values for both fibres. This can be explained by changes in the microstructure (reduction of the pore fraction obtained on initial pyrolysis) and by strain-induced hardening [9, 18, 20]. If this explanation applies, a long-term heat treatment at the testing temperature is expected to reduce the primary creep stage. Therefore, samples of both investigated fibres were heat treated in an argon atmosphere for 15 h at a temperature of 1200 °C. Subsequently, creep experiments in an argon atmosphere were performed as described above.

The results are shown in Fig. 11. In the case of the heat-pretreated samples, a much smaller primary creep could be observed for both fibre types. The expected steady-state creep was not observed. The slow shrinkage indicated by the negative slope of the curves can be attributed to the result of stress-induced hardening. This effect does not depend on the pretreatment indicated by the fact that the slopes of the curves obtained from untreated and heat-pretreated samples have the same values.

4. Conclusion

As mentioned elsewhere [1], the SiC-based fibres are thermodynamically unstable at high temperatures. The strength of Nicalon and Tyranno fibre bundles significantly decreases at temperatures above 500 °C. The decrease in the force at rupture was observed for air and for argon atmospheres at relatively low testing temperatures (about 500 °C). This temperature is very low in comparison with the desired application temperature for ceramic matrix–ceramic fibre composites. For such applications, the mechanical properties are mainly controlled by the mechanical properties of the reinforcing fibres. Primary shrinkage of the fibres could be suppressed by heating the fibres in an argon atmosphere for several hours to their pyrolysis temperature. The creep behaviour of the multifilament bundles is similar to that reported for the monofilaments. Therefore, it was possible to establish a testing method for creep and tensile strength measurements of fibre bundles at temperatures up to 1300 °C in oxidizing or inert gas atmospheres.

Acknowledgements

The authors thank the Institut für Werkstoffkunde I for their assistance in the construction of the furnace. This research is supported by the Bundesminister für Forschung und Technologie (03 M 10568).

References

1. D. J. PYSHER, K. C. GORETTA, R. S. HODDER Jr and R. E. TRESSLER, *J. Am. Ceram. Soc.* **72** (1989) 284.
2. A. S. FAREED, P. FANG, M. J. KOCZAK and F. M. KO, *Am. Ceram. Soc. Bull.* **66** (1987) 353.
3. T. MAH, N. L. HECHT, D. E. McCULLUM, J. R. HOENIGMAN, H. M. KIM, A. P. KATZ and H. A. LIPSITT, *J. Mater. Sci.* **19** (1984) 1191.
4. Ph. SCHRECK, C. VIX-GUTERL, P. EHRBURGER and J. LAHAYE, *ibid.* **27** (1992) 4237.
5. D. J. PYSHER and R. E. TRESSLER, *ibid.* **27** (1992) 423.
6. R. E. TRESSLER and J. A. DICARLO, in "Proceedings of the 6th European Conference on Composite Materials, Bordeaux; EECM-6, Euro-Japanese Colloquium on Ceramic Fibres (eds A. R. Bunsell and I. Kimpara" (1993) pp. 33–49.
7. R. BODET, J. LAMON and R. E. TRESSLER, *ibid.* pp. 75–83.
8. G. SIMON and A. R. BUNSELL, *J. Mater. Sci.* **19** (1984) 3649.
9. *Idem, ibid.* **19** (1984) 3658.
10. D. B. FISCHBACH, P. M. LEMOINE and G. V. YEN, *ibid.* **23** (1988) 987.
11. J. V. VILLENEUVE, D. MOCAER, R. PAILLER, R. NASLAIN and P. OLRY, *ibid.* **28** (1993) 1227.
12. HYOUN-EE KIM and A. J. MOORHEAD, *J. Am. Ceram. Soc.* **74** (1991) 666.
13. M. HUGER, S. SOUCHARD and C. GAULT, *J. Mater. Sci. Lett.* **12** (1993) 414.
14. J. LIPOWITZ, J. A. RABE and R. M. SALINGER, in "International Fiber Science Technology Series 12, 1993, Vol. 3, "High Technology Fibers", Part C" pp. 207–73.
15. B. A. BENDER, J. S. WALLACE and D. J. SCHRODT, *J. Mater. Sci.* **26** (1991) 970.
16. P. LE COUSTUMER, M. MONTHIOUX and A. OBERLIN, *J. Eur. Ceram. Soc.* **11** (1993) 95.
17. J. LIPOWITZ, *Am. Ceram. Soc. Bull.* **70** (1991) 1888.
18. T. SHIMOO, Y. KAKEHI, H. CHEN and K. OKAMURA, *Funtai oyobi Funmatsu Yakin* **39** (1992) 86.
19. D. J. PYSHER, NANYING JIA, R. J. BODET and R. E. TRESSLER, in "High Performance Composites of the 1990's", edited by S. K. Das, C. P. Ballard and F. Marikar (TMS, Warrendale, PA, 1990) pp. 267–81.
20. J. A. DICARLO and G. N. MOSCHER, in "Failure Mechanisms in High Temperature Composite Materials", ASME, AD-Vol. 22/AMD-Vol. 122 (1991) pp. 15–22.

Received 18 January 1994
and accepted 7 June 1995