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Thermomechanical Stability of Nicalon Fibres in a Carbon Monoxide Environment

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Abstract

Microstructural changes and the related strength degradation were investigated for the Nicalon ceramic fibre heat-treated in argon and in a CO/Ar mixture (with a CO partial pressure of 40 kPa) at 1200–1400°C and for different periods of time (0·5–30 h). Detailed structural and compositional analyses were carried out using X-ray diffraction, TEM, SEM, and Auger electron spectroscopy. Strength degradation of the Nicalon fibre after heat-treatments in argon resulted from the fibre decomposition and CO gas escape which produced surface defects, grain growth and intergranular porosity. On the other hand, the strength degradation was effectively reduced for fibres heat-treated in an appropriate atmosphere of argon and CO, as long as the heat-treatment temperature was kept below 1400°C. Such conditions of heat-treatment in CO/Ar showed little effect on the grain size.

1 Introduction

Commercially available and developmental ceramic fibres are stimulating extensive research on the fabrication of ceramic and metal matrix composites for high temperature applications. To determine whether or not the composites can first be produced and then successfully used in a high temperature environment, the microstructure, microchemistry, mechanical properties, and thermal stability of the fibres are important parameters that need to be characterized. This characterization also provides information which will help to develop appropriate processes to produce fibres for high temperature use. There have been many studies of the effects of thermal exposure on the properties of polymer derived ceramic fibres, especially on Nicalon[†] Si–C–O fibres. It is now clear from the literature that the major factors which will influence the mechanical properties of these fibres at high temperature are microstructural instability and surface reaction. The thermodynamic calculations performed by Luthra[1] and Greil[2] indicate that the Nicalon fibre is inherently unstable at high temperatures, and other investigators[3] have proposed that the ternary amorphous SiO_xC_y phase in Nicalon would be primarily responsible for this instability. The decomposition of the silicon oxycarbide phase in the Nicalon fibre[4–6] and in other polycarbosilane based ceramics[7] results in weight loss associated with CO(g) and perhaps SiO(g) evolution and β-SiC grain growth. With or without involvement of excess carbon, this decomposition will result in the formation of gas and SiC. This means that one can anticipate the following reactions to take place in fibres at high temperature and, essentially, in any environment:

$$SiO_xC_y(a) \rightarrow n_{SiC}SiC(s) + n_{CO}\,CO(g) + n_{SiO}\,SiO(g) \qquad (1)$$

or

$$SiO_xC_y(a) + C(s) \rightarrow n_{SiC}\,SiC(s) + n_{CO}\,CO(g) + n_{SiO}\,SiO(g) \qquad (2)$$

and

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO(g) \qquad (3)$$

According to eqns (1)–(3), the decomposition, crystallization, and gas evolution must occur simultaneously. If one of them can be suppressed, it should suppress them all, until all the SiO_xC_y species reach an equilibrium. A strong support for this assumption can be found from fibres heat-treated under various pressures. Jaskowiak *et al.*[8]

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noticed that under vacuum or at normal pressure, both rapid weight loss and grain growth of Nicalon fibres start at 1200°C. A strong correlation between the grain growth and weight loss was observed. While oxidizing CVD SiC powder, Pampuch *et al.*[3,9] observed a ternary phase of Si, C, and O which was only stable for oxidation temperatures below 1200°C. It decomposed to SiO_2 and Si with the evolution of CO(g) at higher temperatures. Mah *et al.*[4] studied the decomposition of Nicalon, and the major out-gassing species was CO(g). Johnson *et al.*[5] measured the partial pressure of gases over Nicalon, and the major vaporization species were SiO(g) and CO(g). Previous investigations[10] had shown that grain growth and porosity increased with time of heat-treatment at 1300°C. Recently, the high temperature creep behavior of these fibres in argon has been characterized by a rheological model based on the viscous flow of a concentrated suspension of SiC particles in an unstable viscoelastic matrix. As a result of the decomposition of the SiO_xC_y phase, the viscosity of the fibre increased which caused the continuously decreasing creep rate and the steady-state creep impossible under such conditions.[11]

Considering the instability of Nicalon fibre leads to an important question: could the decomposition of SiO_xC_y be stopped? Two methods have proved to be effective in reducing the decomposition of SiO_xC_y: high total pressures and a carbon monoxide partial pressure. The first method was used by Jaskowiak and DiCarlo,[8] and Jaskowiak[12] with high pressure argon and nitrogen gas. However, the decomposition of the ternary phase occurred again when the high pressure argon heat-treated fibre was subsequently reheated at normal argon pressure. The second method attempted by Bibbo *et al.*[13] involves treatments of Nicalon in argon/CO mixtures with a range of CO partial pressures. A maximum effect on the strength of the fibre was found for pCO = 0·4 atm after a 30 min heat-treatment at 1300°C. However, no microstructural characterization was performed in this study. Bender *et al.*[14] have also mentioned the benefits of CO treatments (P_{CO} = 1 atm). After 3 h at 1600°C, the Nicalon fibre retained an average strength close to 1·4 GPa whereas in nitrogen at the same temperature the fibre retained less than 5% of its original strength. Bender *et al.* showed that the fibre underwent few microstructural changes in CO, i.e. limited grain growth and the beginning of the development of microporosity.

The purpose of the study was to investigate the long-term thermomechanical behavior of Nicalon fibres in a so-called chemically stable environment, i.e. by achievement of the fibre stability via suppressing SiO_xC_y decomposition and grain growth during heat-treatments in flowing CO. The results of these experiments helped to further establish the steady-state creep behavior of those fibres.[15]

2 Experimental Procedure

2.1 Material

The thermomechanical stability of Nicalon was investigated on a ceramic grade type fibre,[†] obtained from a polycarbosilane precursor. The Nicalon fibre contains Si, C, O as its major elements and some traces of hydrogen in it have been also reported.[16] Nicalon NLP 201 is a nanocrystalline β-SiC based-fibre. It has an average diameter of 15 μm. The fibres were received in spool form and coated with an epoxy sizing. This sizing was removed prior to the mechanical and structural characterization by washing the fibre bundle in ultrasonically agitated baths of acetone, ethyl alcohol and distilled water, successively, except for those exposed to high temperature treatments which were kept for 1 h at 550°C under vacuum prior to the temperature raise. Traces of carbon resulting from the sizing decomposition were detected by Auger analysis on the surface of the thermally desized fibres. It was verified that this method of desizing does not influence the initial strength distribution of the as-received fibres.

2.2 Heat-treatment furnaces and procedures

The custom built furnace used for the argon heat-treatments consisted of a vertical alumina tube heated by six SiC heating elements. Temperature was maintained via a controller and monitored using a Pt/Pt–10% Rh thermocouple located near the outer surface of the alumina tube and in the center of the hot zone. Fibre bundles were suspended by sewing them through a carbon cloth placed inside the cold, top part of the tube. A preliminary step consisting of vacuuming the furnace (down to $\approx 10^{-1}$ Pa) was performed at the beginning of the heat-treatment (up to 550°C). A first dwell time for at least 45 min (sometimes up to 2 h) with flowing UHP argon gas (oxygen $< 10^{-9}$ ppm) at 550°C was programmed prior to the final ramp. This was used to burn off the sizing. An in-line oxygen sensor (zirconia cell) connected to a voltmeter for a better accuracy was used to determine the oxygen level. As the temperature rose, the sensor indicated a decrease in the oxygen content. Different equipment was used for heat-treating

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[†] Ceramic grade NLP 201.

Nicalon fibres at elevated temperatures in a very specific CO/Ar atmosphere (P_{CO} = 40 kPa). The apparatus used to heat up to 1200°C was a thermogravimetric balance consisting of a vertical fused quartz tube over which a furnace could slide. Fibre bundles were bound together by using an extra fibre bundle and were suspended in the tube by a silica hook to a platinum wire. The furnace was then raised and heat-treatment temperatures were reached within 30 min. A high temperature/atmosphere controlled tube furnace was used for heat-treating Nicalon fibres in CO at higher temperatures. Fibres were placed in a SiC boat and heated at 30°C min^{-1} in a horizontal alumina tube using Super Kanthal elements. Both furnace setups utilized mass flow controllers for the exact control of gaseous species entering the furnace tube. While the total pressure of the gases remained at one atmosphere, the partial pressures of individual gases (argon and carbon monoxide) could be adjusted through the flow-rate control of the mass flow controllers. The flow rate was adjusted to 5 standard cm^3 min^{-1}. Oxygen degassing was accomplished prior to each run by flowing argon for 30 min, and pre- and post-furnace oxygen traces were detected with an in-line zirconia cell.

2.3 Materials characterization

X-ray diffraction patterns were generated with a diffractometer* using Cu-Kα radiation. As-received and heat-treated fibres were ground into powder using an alumina mortar and pestle. Grinding was performed in acetone. The peaks in the diffraction patterns were identified using the JCPDS† files.

Auger electron analyses were performed with an AES microanalyser†† using the depth profiling mode on CO-heat-treated fibre samples mounted on indium foil. The spectra were recorded from the filament surfaces (spot size ~ 1 μm). The intensities of selected Auger electron transitions, (i.e. LVV for silicon, KLL for carbon, and KLL for oxygen) were recorded as a function of the thickness of the material which has been sputtered (established for a Ta_2O_5 standard).

Individual filament fracture surfaces after strength tests and surface degradation after heat-treatments were examined in a scanning electron microscope.[a]

TEM analyses were obtained with a 120 kV microscope.[b] The three main techniques of conventional TEM, i.e. bright field imaging (BF), dark field imaging (DF), and selected area diffraction (SAD), were used to characterize the fibre microstructure. TEM specimen preparation used two complementary techniques, i.e. ion milling to obtain longitudinal sections of the fibre core and microtomy to get cross-sections for the information concerning the fibre surface. The ion milling technique was performed using a dual ion mill,[c] whereas thin sections of fibres first embedded in a resin were cut using a diamond knife[d] and mounted on microtome.[e]

2.4 Strength tests

The room temperature strength tests on Nicalon fibres were performed on a table-top tester[f] with a small capacity Type A load cell (10, 20, 50 g full scale). Gripping of the filament was accomplished by mounting the fibre ends to paper tabs with epoxy. High temperature tests were performed in a small, custom-built furnace (Kanthal heating elements) using the same apparatus and the same cold gripping technique. All high temperature tests were begun within about 1 min after temperature stabilization because the furnace slit made the fibre loading easier. To determine fibre diameter, a portion of the test fibre was placed on a microscope slide and examined using an optical microscope.[g] All fibres were tested at the same cross-head speed of 0·5 mm/min, corresponding to a strain rate of 3·28 10^{-4} s^{-1} for the 25·4 mm gauge length for room temperature strength tests, and 5·56 10^{-5} s^{-1} for the 152·4 mm gauge length for the high temperature tests.

3 Results and Discussion

3.1 Microstructural analyses

Microstructural analyses were performed using TEM and XRD. Figure 1 represents the XRD spectra for fibres heat-treated at 1300°C at 0 and 40 kPa of CO, respectively. In the pure argon, SiC crystallization increased with time of heat-treatment, as seen in Fig. 1(a). Although image analysis using TEM dark field is not a reliable technique for ceramics containing very small grain sizes, it was just used here to evidence an increase of the

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†Joint Committee on Powder Diffraction Standards, Swarthmore, PA, USA.

††Model PHI-590 SAM, Perking-Elmer Corp., Norwalk, CT, USA.

[a] Model SX-40A, International Scientific Instruments, Santa Clara, CA, USA.

[b] Model 420 T, Philips Electronic Instruments Inc., Mahwah, NJ, USA.

[c] Gatan Inc., Warrendales, PA, USA.

[d] E.I. du Pond de Nemours, Wilmington, De, USA.

[e] Microtome, Inc., Sweden.

[f] Model 1102, Instron Corp., Canton, MA, USA.

[g] Bausch and Lomb, Rochester, NY, USA

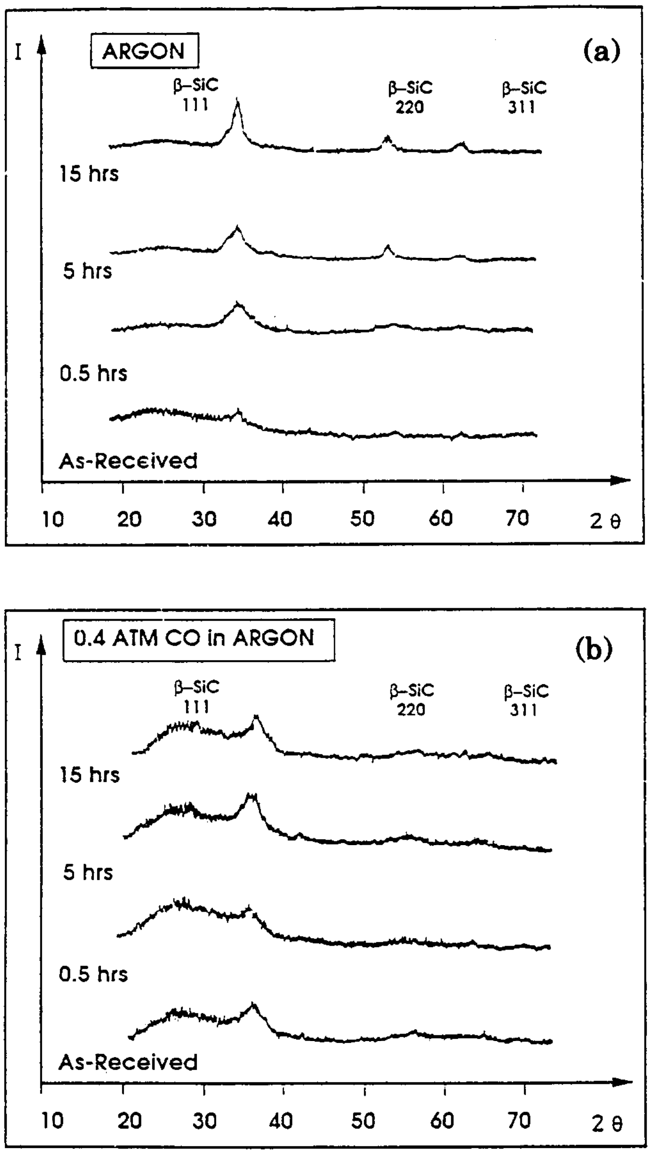

Fig. 1. XRD analysis of argon/CO heat-treated Nicalon fibres as a function of heat treatment time at partial pressures of CO of (a) 0 kPa and (b) 40 kPa.

mean β-SiC grain size in Nicalon as a function of the heat-treatment time in argon. The mean grain size changed from 2·7 nm in the as-received fibre to ~10 nm after 15 h at 1300°C in argon. Figure 2 shows the grain growth and porosity resulting from this heat-treatment. It was previously mentioned that β-SiC grain growth could arise from SiO_xC_y decomposition, according to eqns (1)–(3). If one can assume that the escape of gas species, (i.e. CO or/and SiO) is faster near the fibre surface than near the center, one will assume that the same will be true for the grain growth. Thus decomposition and related grain growth will proceed further in the fibre with time of heat-treatment. On the other hand, the structural stability of Nicalon fibres was greatly enhanced when heat-treated at 1300°C with CO partial pressure of 40 kPa, as evidenced in Fig. 1(b). Figure 3, through a series of TEM micrographs of fibre cross-sections, shows evidence of carbon build-up on the Nicalon fibre. The two micrographs in Figs 3(a) and (b) indicate that carbon actually formed layers stacked parallel to the fibre surface. Figure 3(c) shows the turbostratic structure of this carbon, and the 004 reflection on the SAD pattern (inset of Fig. 3(c)) shows its orientation. The thickness of this carbon layer is about 500 nm. This carbon deposit may arise from the decomposition of CO(g) into C(s) and CO_2(g) during the cooling of the chamber at the end of the heat-treatment.

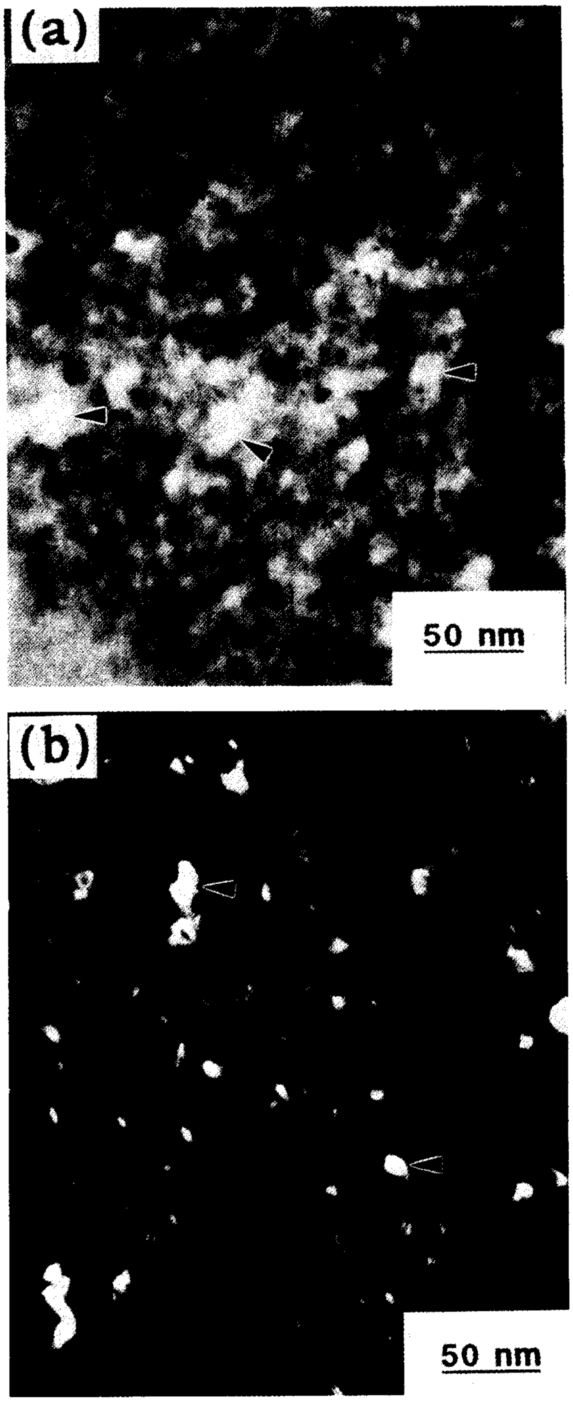

Fig. 2. BF and associated 111-SiC DF image of the cross section of a Nicalon fibre heat-treated in pure argon at 1300°C for 15 h showing (a) evidence of porosity and (b) grain growth, as indicated by arrows.

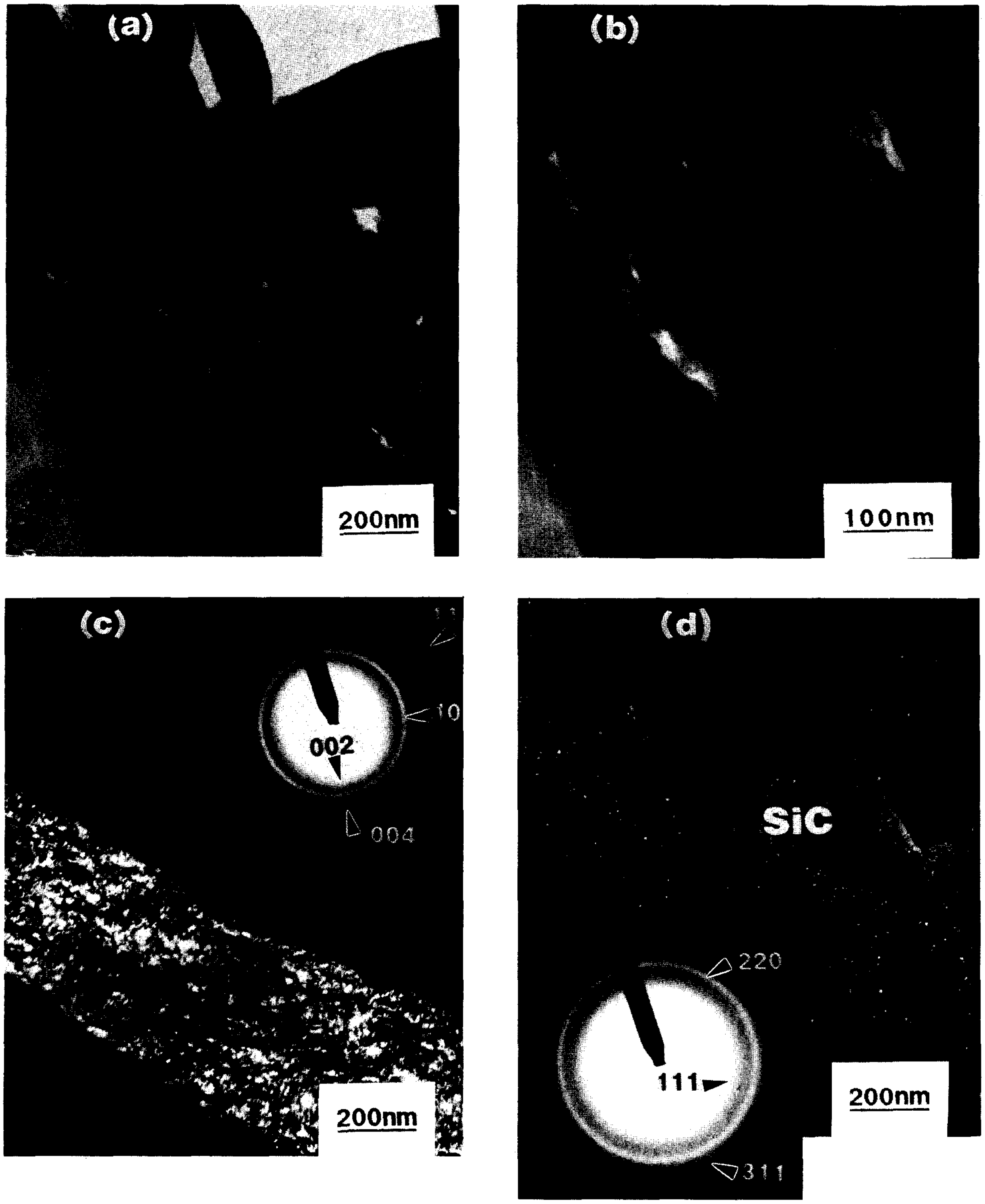

Fig. 3. TEM analysis of a CO heat-treated Nicalon fibre at 1300°C for 15 h. (a) and (b) are BF micrographs of the fibre surface, (c) and (d) are DF and SAD patterns of (c) carbon and (d) SiC.

Bibbo *et al.*[13] also observed a build-up of carbon on the fibre surface in the case of a 1 h heat-treatment at 1300°C. The thickness of this carbon layer was seen to increase with the initial CO partial pressure. The SiC-111 dark field image, in Fig. 3(d), shows that little grain growth occurred after 15 h at 1300°C in 40 kPa of CO, indicating that the thermal decomposition of the fibre could be indeed minimized in 40 kPa CO. Fibres heat-treated at 1200°C behaved similarly. An example of a fibre surface is seen in Fig. 4. The previous figures, for fibres that were heat-treated at 1300°C, can be compared with Fig. 5, for fibres heat-treated at 1400°C at the same partial pressure of CO. Figure 5 indicates that, despite the presence of carbon build-up on the fibre surface (see arrows in Fig. 5(a)), an extensive crystallization of SiC occurred at higher temperatures, which showed no

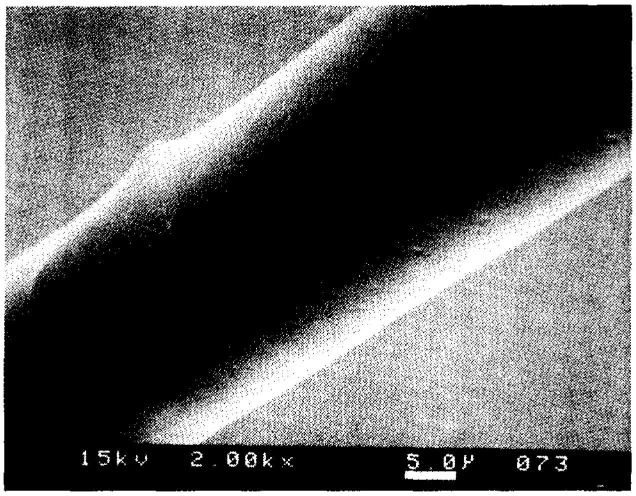

Fig. 4. SEM micrograph of a Nicalon fibre heat-treated in CO (40 kPa) at 1200°C for 0·5 h.

difference with heat-treatments in pure argon.[10] The spotty rings on the SAD pattern correspond to well developed SiC grains beneath the carbon. Some cracks are also apparent on the bright field micrograph in Fig. 5(a). It is unsure whether these cracks preexist or originate from the TEM specimen preparation. Internal pressure in the fibre is likely to build-up until the gas products resulting from fibre decomposition are released, causing a network of cracks beneath the carbon sheath. During the cutting operation by microtomy, the diamond knife can also induce damage in the degraded fibre by relieving these internal stresses. A well-developed crack network has been observed in fully decomposed fibres after prolonged heat-treatments in pure argon.[10] Because of the difference in textures (which behave differently regarding the stresses induced by the diamond knife) the cracks apparently vanish in a ≈ 400 nm wide region of different contrast, intermediate between the outer carbon layer and the fibre bulk. Figure 5(b) shows that the SiC grains are smaller in this transition region (indicated by double arrows) than those in the fibre bulk. This could be explained by a carbon penetration, which inhibited grain growth in the fibre surface. The microstructural changes that Nicalon underwent from 1300 to 1400°C while the partial pressure of CO was maintained at 40 kPa can be explained through thermodynamic calculations. Luthra[1] has shown that the equilibrium CO partial pressure above Si–C–O fibres at 1400°C is close to 100 kPa. Thus, it is believed that the exposure of the fibre at 1400°C to an environment containing a lower CO partial pressure than this equilibrium partial pressure will result in a more pronounced degradation of the fibre microstructure, (i.e. grain growth, porosity and gas evolution).

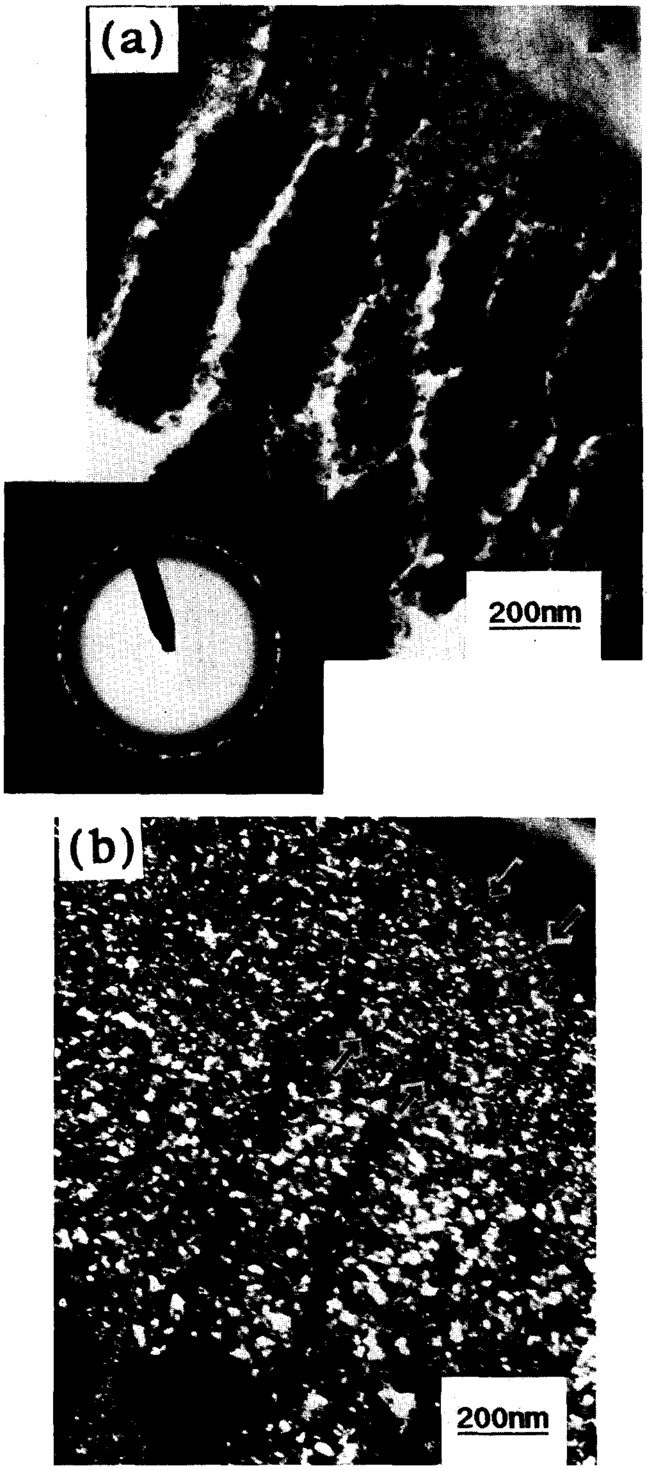

Fig. 5. TEM analysis of a CO heat-treated Nicalon fibre at 1400°C for 5 h. (a) BF micrograph of the fibre surface and SAD pattern. Single arrow shows the carbon layer. (b) DF of SiC. Double arrows show the region of limited grain growth.

3.2 Scanning auger electron analyses

SAM analyses were performed on Nicalon fibres to evaluate more precisely the composition change resulting from surface reactions occurring after heat-treatment in CO/Ar. Results of surface composition for heat-treatments performed at 1300°C for 15 h, and at 1400°C for 5 h, both at the same partial pressure of 40 kPa, are shown in Fig. 6

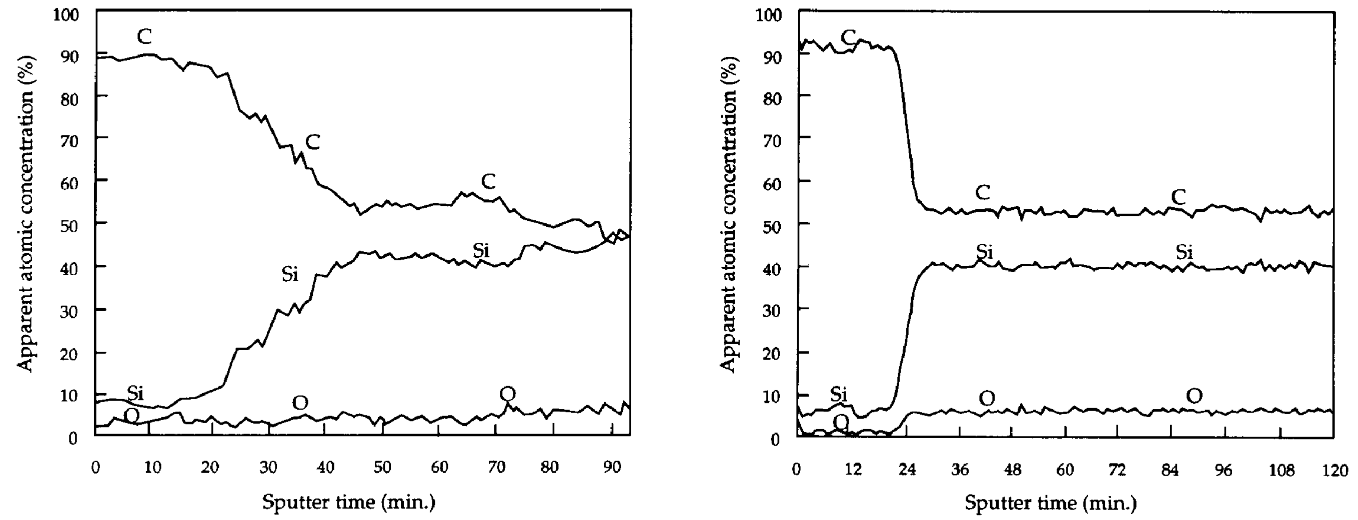

Fig. 6. AES analyses on Nicalon fibres after heat-treatment in CO and argon at CO partial pressure of 40 kPa. Fibres were heat-treated at (a) 1400°C for 5 h and (b) 1300°C for 15 h. Profiles show a carbon build-up on the surface (sputtering rate 25 nm/min; reference Ta_2O_5).

(a),(b). Both fibres developed a carbon rich layer of about 0·45 μm on their surface, according to an estimated sputtering rate of 25 nm/min (notice that this result agrees well with the TEM analysis in Fig. 3(c)). However, the sample heated at 1400°C did not show a sudden change in the composition profile compared to the other specimen. Instead, the carbon was found to decrease progressively with depth while at the same time silicon, probably as SiC, was increasing. On the other hand, the sample heated at 1300°C had a stable composition beneath the build-up of carbon. Moreover, this sub-layer composition was found to match that of the as-received fibre, i.e. 40 at% (Si), 53 at% (C), and 7 at% (O), proof that decomposition had been suppressed. After heat-treatment in the CO atmosphere at 1300°C, there was in fact only a deposition of carbon on the surface of the fibres.

3.3 Effect of heat-treatment on fibre strength

Room temperature strength tests were performed on heat-treated Nicalon fibres in CO/Ar at 0 and 40 kPa of CO. Results are reported in Table 1. In Fig. 7(a), the strength of Nicalon fibres at room temperature is plotted versus time of exposure in various environments, and follows a logarithmic decay for all heat-treatment conditions. The effect of CO partial pressure on the fibre stability is obvious. Fibres heat-treated in the CO/Ar mixture exhibit much less strength reduction compared to those heat-treated in pure argon. After a 30 h heat-treatment at 1200°C in CO, the Nicalon fibre exhibited only a 25% loss in strength, while for the

Table 1. Room temperature tensile strength and modulus of as-received and argon/CO heat treated Nicalon fibres versus heat treatment time

Heat treatment temperature (°C)	*Partial pressure CO (kPa)*	*Heat treatment time (h)*	*Number of fibres tested*	*Tensile strength (MPa)*	*Standard deviation (MPa)*	*Strength retention (%)*	*Young's modulus (GPa)*	*Standard deviation (GPa)*
—	—	—	15	2262	445	—	233	32
1000	0	15	12	1830	465	81	205	34
		30	12	1623	456	72	171	25
1200	0	15	10	1204	187	53	183	17
		30	9	743	652	33	165	46
1300	0	0·5	17	1241	404	55	206	25
		5	14	964	591	43	214	58
		15	12	545	189	24	180	34
		30	11	363	234	16	145	67
1400	0	2	5	818	556	36	186	9
		15	9	211	83	9	85	12
1200	40	0·5	14	1826	521	81	254	57
		5	16	1764	748	78	225	51
		15	17	1633	399	72	207	22
		30	10	1642	341	73	218	32
1300	40	0·5	13	2023	283	89	218	49
		5	17	1762	468	78	193	52
		15	15	1710	516	76	209	48

same temperature and time in argon, the loss was close to 70%. When comparing the data for a 15 h treatment at 1300°C, the losses became 22 and 76%, for CO and pure argon heat-treatments, respectively. The effect of argon and CO annealing treatments on the elastic modulus is shown in Fig. 7(b). Whereas the Young's modulus decreased from 230 to 160 GPa after 30 h at 1200°C in argon (the drop is even more drastic at 1300°C), its value never dropped below 200 GPa in CO. The observed increase after about 15 h at 1200°C and after only a few hours at 1300°C was probably due to the high stiffness of the fibre surface since a thick and oriented carbon layer ((001) carbon planes parallel to the surface) developed on the fibre surface. Figure 8 is an SEM micrograph of the fracture surface of a Nicalon fibre heat-treated at 1200°C for 0·5 h. The fibre had a rupture strength (2010 MPa) slightly above the average (1820 MPa). A notable feature observed on this figure as well as on other fracture surfaces is the evidence of debonding of the carbon layer. In some cases, fracture originated from bubbles beneath the carbon sheath perhaps because gaseous species generated by some late local decomposition

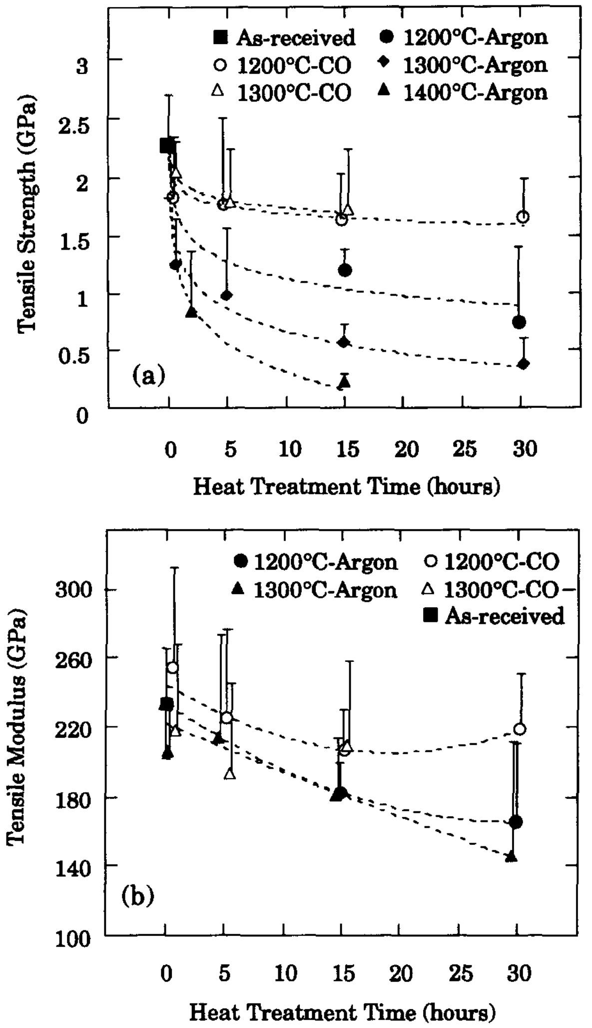

Fig. 7. Effect of CO and argon heat-treatments on (a) the rupture strength and (b) the Young's modulus of Nicalon at room temperature. The single sided bars represent the standard deviations.

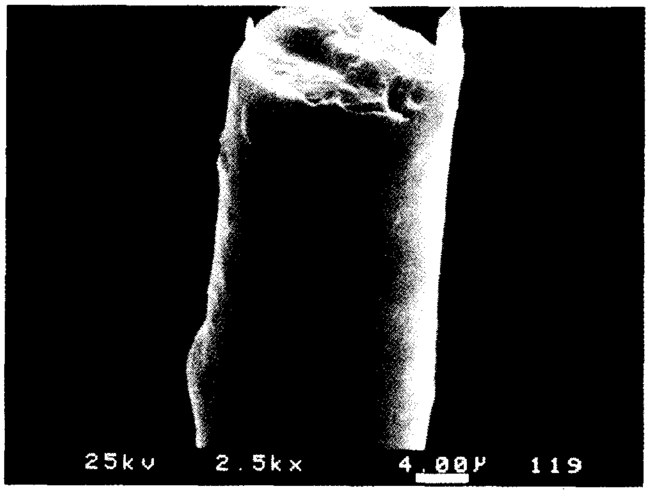

Fig. 8. Fracture surface of a Nicalon filament tested at room temperature after the fibre was heat treated in CO/Ar (P_{CO} = 40 kPa, T = 1200°C, t = 0·5 h). The fibre had a strength of 2010 MPa (standard deviation = 533 MPa, 14 tests, average strength = 1820 MPa).

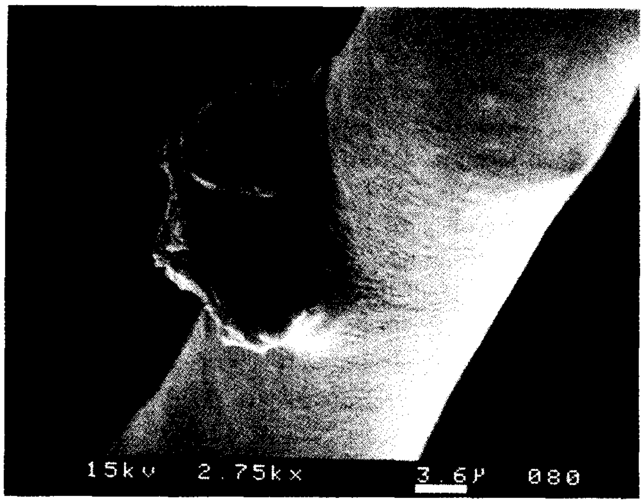

Fig. 9. SEM micrograph of a Nicalon fibre heat-treated in CO (40 kPa) at 1300°C for 5 h showing local surface decomposition.

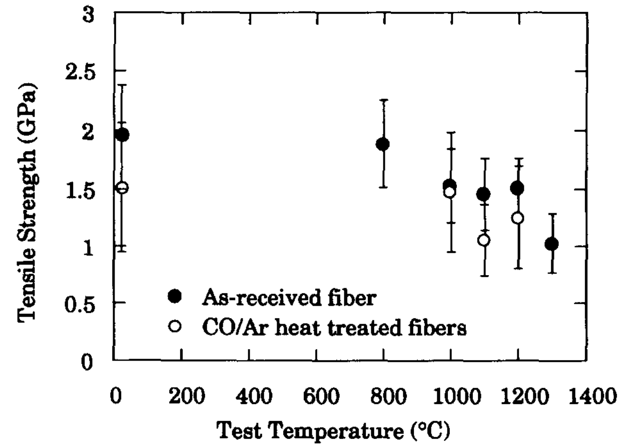

Fig. 10. Effect of CO treatments on the short term strength of Nicalon fibres at high temperatures. The error bars represent the standard deviation.

Table 2. Short term strength tests on as-received and CO/Ar heat-treated Nicalon fibres in air at high temperature[¶]

	As-Received			*CO/Ar Heat Treated*		
T[¶¶] (°C)	σu[†] (GPa)	*stD*σ[††] (GPa)	*n*[§]	σ_u (GPa)	*stD*σ (GPa)	*n*
1000	1·53	0·30	10	1·47	0·51	11
1100	1·46	0·30	10	1·06	0·31	4
1200	1·51	0·25	10	1·25	0·44	5

[¶] Condition of heat treatment: pCO +pAr = 1 atm, T = 1200°C, *t* = 20 h.
[¶¶] Testing temperature.
[†] Mean strength.
[††] Standard deviation.
[§] Number of specimens tested.

had been stopped by the carbon build-up (Fig. 9). This rare feature of the heat-treated fibres was never observed on the as-received fibres.

High temperature strength tests were performed in air on as-received Nicalon fibres as well as on those that were annealed in CO/Ar at 1200°C for 30 h. Results shown in Fig. 10 and reported in Table 2 indicate that the two sets of fibres have lost part of their strengths at high temperatures. A slightly greater strength loss is sometimes observed for the fibres previously annealed in CO/Ar, which might be related to the exposure of the defectuous surface of the fibres to oxidation after the carbon sheath was burned off.

4 Conclusions

The goal of CO treatments was to investigate the feasibility of suppressing the Nicalon fibre decomposition and more precisely to evaluate the effects of the long term and temperature variation of such annealing treatments on the thermochemical stability and the strength of the fibre. Heat-treatments at 40 kPa of CO in argon were performed in the range 1200–1400°C at times between 0·5 and 30 h. At the end of the heat-treatment, the reduction of CO from the atmosphere during the cooling of the furnace always formed a carbon-rich layer on the fibre surface. Little effect of the CO heat-treatments on the grain size was found up to 1300°C, but extensive crystallization, with ~60 nm large grains, and pronounced porosity were observed at 1400°C. An intermediate carbon-rich region with limited SiC grain growth was found beneath the carbon layer at the highest temperature. The strength degradation could be effectively reduced for Nicalon fibres heat-treated at 1200 and 1300°C in Ar/CO, with a CO partial pressure of 40 kPa. However, this gas mixture was no longer effective in preserving fibre strength when heat-treated at higher temperatures. Part of this investigation confirm the results of other authors that the presence of oxygen-rich phases inside PCS-derived fibres is responsible for the degradation of their thermo-mechanical properties. The Si–C–O fibre is inherently unstable in air and argon beyond about 1200°C but its decomposition can be delayed at higher temperatures in an atmosphere of carbon monoxide as long as the CO partial pressure is high enough. Additional studies on the fibre behavior in CO are presently being done to characterize their intrinsic creep-rupture properties.

Acknowledgements

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