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Reactivity and molecular structure of silicon carbide fibres derived from polycarbosilanes

Part I *Thermal behaviour and reactivity*

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The thermal behaviour of Nicalon NML 202 fibres was carried out in the absence and in the presence of oxygen. The gaseous species produced and the oxygen balance were determined with a mass spectrometer. Three samples were studied: the desized initial fibre, this fibre after treatment with hydrofluoric acid, and a polycrystalline silicon carbide powder. It was shown that (i) the initial fibre has still an organic character, (ii) it contains a silica-rich layer, and (iii) beneath the silica-rich sheath the bulk of the fibre contains free carbon embedded in a silicon carbide-based network.

1. Introduction

In the aeronautical and space industries, materials are usually required to keep their mechanical properties at elevated temperatures in the presence of oxidation agents. For many uses, ceramic fibre-reinforced composites are promising materials. Ceramic fibres can be obtained by thermal treatment of organometallic polymers [1], in a way similar to the preparation of ex-polyacrylonitrile carbon fibres [2]. The structure of the so-called ceramic fibres from organometallic precursors is quite complex [3–5] and the properties are often intermediate between those of inorganic and polymeric materials.

The silicon carbide fibre Nicalon NML202 (Nippon Carbon Co. Ltd, Tokyo) obtained by pyrolysis of a polycarbosilane-type precursor, besides SiC, contains an excess of carbon and oxygen [6]. The stability of the fibre and its thermomechanical properties strongly decline above 1400 K [7–13]. This degradation has been correlated with chemical and structural evolutions of the fibre at high temperature [9] as well as with the build-up of a silica surface film [10]. The properties of the fibres at temperature below 1270 K are not well known although they control the surface characteristics of the materials. In particular the incorporation of ceramic fibres in metal matrices requires a good understanding of their surface properties. Since the silicon carbide-based fibre contains a large excess of carbon, it is of prime importance to determine its reactivity with oxygen in relationship with its structure.

Yajima [6], from a morphological study of the fibre by phase-contrast electron microscopy, concluded that the carbon in excess is present as small domains uniformly distributed between β-SiC domains and exhibits a low reactivity. From more recent work [14], it is concluded that carbon in excess corresponds to very small flat polyaromatic structures, randomly distributed in the fibre.

The presence of carbon at the fibre surface may also originate from the thermal decomposition of sizing compounds. Removal of the carbon by oxidative treatments may affect the surface properties of the fibres and also promote the formation of a silica layer with different surface characteristics.

The purpose of the present paper is to study the thermal behaviour of the SiC-based fibre in inert and oxidizing atmospheres. In particular the reactivity of the fibre with oxygen at temperatures below 1270 K will be investigated by following the uptake of oxygen and the gasification of carbon.

2. Experimental procedure

2.1. Samples and sample preparation

A commercially produced SiC-based fibre has been studied. The atomic composition of the fibre is Si 35%, C 52%, O 13%, which corresponds to a hypothetical calculated composition of SiC 65%, C 16%, SiO_2 25% (mol %) [15]. The as-received fibre has a polyvinyl acetate sizing. The sizing is removed from the fibre by extraction at 352.6 K with methylethylketone (MEK) during 48 h in a Soxhlet apparatus and subsequent thermolysis at 700 K in an argon atmosphere for 4 h, prior to a new extraction with MEK during 24 h. The fibre is dried at 370 K in air during one night after each extraction. The weight loss of the samples after desizing corresponds to 1.1 ± 0.5%. Some fibres are subsequently treated in a diluted (20 vol %) hydrofluoric acid (HF) bath during 2 h in order to eliminate

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an oxide-rich layer on their surface. Fibres are abundantly washed with demineralized water after HF treatment.

A polycrystalline silicon carbide powder (SiC 99.3 wt %, C < 0.1 wt %) is also studied to compare the results for the SiC-based fibres with those for mineral silicon carbide.

The specific surface area of the samples is measured by adsorption of Kr at 77 K according to the BET method. In all cases the samples are degassed at 470 K for 14 h before Kr adsorption.

2.2. Methods of characterization

2.2.1. Vacuum desorption

Temperature-programmed desorption (TPD) experiments are carried out in vacuum using fused silica glass tube and crucibles for temperatures below 1270 K and alumina tube and crucibles for higher temperatures. The linear heating rate is fixed to 200 K h^{-1}. Evacuation is performed using diffusion and turbomolecular pumping units achieving a dynamic vacuum better than 10^{-5} Pa. Evolved gaseous species are dynamically analysed with a quadrupolar mass spectrometer (Balzers QMG 112). In a typical run, about 2 g of material are used. The number of moles of a given evolved gas is calculated versus heat-treatment temperature from the measurement of its partial pressures, assuming ideal gas behaviour and constant pumping rate in the pressure range investigated. Determination of the partial pressure is made after individual calibration of the mass spectrometer for several gases (H_2O, H_2, CO, CO_2, O_2, N_2, CH_4 and C_2H_4).

2.2.2. Oxygen chemisorption

Oxygen chemisorption experiments are carried out in a volumetric system using about 2 g of sample (volume of the system: about 2.5 l). After degassing at 1220 K for 3 h the sample is exposed to oxygen for 16 h at 570 K under an initial oxygen pressure of 66.5 ± 0.1 Pa. The total pressure in the system is measured with a pressure sensor (Barocel Datametrics, pressure range 0–130 Pa). With these conditions it is assumed that oxidation of silicon carbide can be neglected and will not interfere with the formation of oxygen complexes on carbon species. The chemisorbed complexes are then recovered as CO and CO_2 by subsequent outgassing of the sample under a static vacuum from 570 to 1220 K. The amounts of CO and CO_2 evolved during outgassing are measured volumetrically using mass spectrometry.

2.2.3. Oxidative treatment

Oxidation is carried out in the same volumetric system previously described for oxygen chemisorption measurements. Oxidation is done at 970 K since the TPD studies have shown that the SiC-based fibre does not undergo any measurable chemical change during thermal treatment at 970 K. Typically about 2 g of sample is introduced at room temperature in the silica glass tube and the temperature is raised up to 970 K in a vacuum (total pressure less than 10^{-5} Pa). An oxygen pressure of 66.5 ± 0.1 Pa is then introduced into the volumetric system. This corresponds to 75×10^{-6} mol of oxygen. Changes in the total pressure are measured by a pressure gauge and partial pressures are then determined by measurement of the gaseous composition of the volumetric system using mass spectrometry. The number of moles of the oxidation products is finally calculated using an ideal gas behaviour assumption. For periods of oxidation exceeding 15 h a significant consumption of oxygen is found since more than 80% of the oxygen initially introduced has reacted. At this stage the system is degassed and a second oxidation run is undertaken. It will be seen that the oxidation rate of the sample is not affected.

3. Results

3.1. Thermal treatment

TPD was carried out in a vacuum on the as-received fibres and bundles desized by treatment with MEK. TPD curves corresponding to the desized fibres are shown in Fig. 1. It is seen that above 570 K the main gases produced are carbon monoxide, carbon dioxide, methane and ethylene. The rates of evolution of CO_2 and CH_4 become negligible above 1170 K whereas the rate of CO evolution increases steadily. The desorption rate of C_2H_4 tends to remain nearly constant. Above 1170 K, H_2 is also observed as shown in Fig. 2 which indicates the cumulative amount of evolved H_2 during a TPD experiment. At 1470 K, essentially

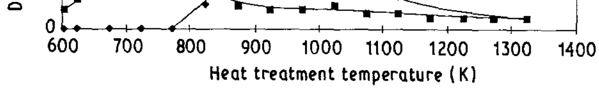

Figure 1 Heat treatment of the desized SiC-based fibre: (◆) CO, (◇) CO_2, (■) CH_4, (□) C_2H_4. Heating rate 200 K h^{-1}

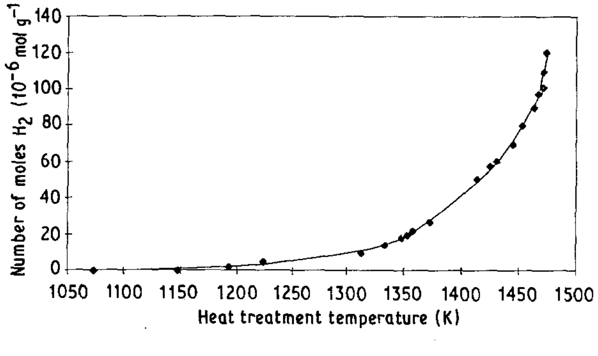

Figure 2 Cumulative amount of hydrogen released during heat treatment under vacuum.

H_2 is released from the fibre. The evolution of H_2 was further investigated during isothermal treatment at 1470 K as indicated in Fig. 3. It is seen that 750 μmol g^{-1} of H_2 have been formed after 6 h of treatment. Although the corresponding weight loss is rather small, the evolution of H_2 indicates a deep change in the molecular composition of the fibre during pyrolysis.

TPD curves of as-received fibres are shown in Fig. 4. The comparison of these curves with those of Fig. 1 shows that the same gases are formed in both cases. Some differences can, however, be seen. In particular the thermal breakdown of the sizing compounds leads to a pronounced gas release in the temperature range 670–870 K and the overall amount of evolved gases is much higher for the as-received fibres. The cumulative amount of desorbed gases in the temperature range 570–1370 K is indicated in Table I for both types of fibre. It is noted that the release of H_2 is not significantly affected by the sizing removal treatment. This fact suggests that the formation of H_2 is not linked to sizing compounds but rather to an intrinsic chemical property of the SiC-based fibre. In contrast, the small amounts of other gases released from the desized fibre may originate either from traces of sizing or solvent left after the MEK extraction treatment or from the fibre itself. The weight loss upon pyrolysis of the as-received fibre (see Table I) is much smaller than that obtained by the sizing removal we have used (1.1 ± 0.5%).

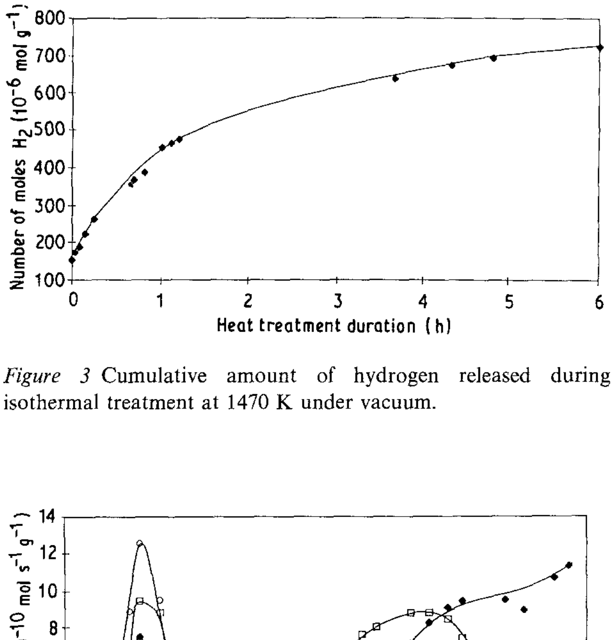

Figure 3 Cumulative amount of hydrogen released during isothermal treatment at 1470 K under vacuum.

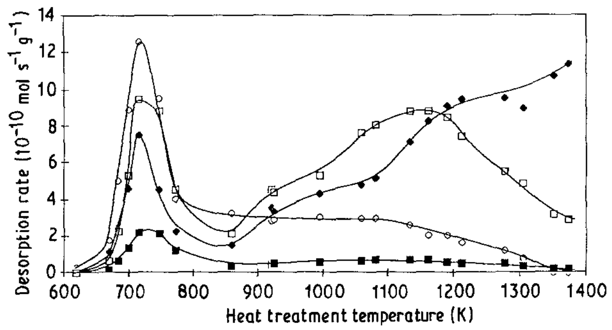

Figure 4 Heat treatment of the sized SiC-based fibre: (◆) CO, (◇) CO_2, (■) CH_4, (□) C_2H_4. Heating rate 200 K h^{-1}

TABLE I Amounts of gases released during thermal treatment of the fibre under vacuum up to 1370 K

Fibre	Gas released (μmol g^{-1})					Weight loss (%)
	CO	CO_2	CH_4	C_2H_4	H_2	
As-received	7.4	4.8	0.9	7.4	27.2	0.07
Desized	1.1	1.5	0.3	0.9	25.0	0.01

3.2. Chemisorption of oxygen at 573 K

As already mentioned, SiC-based fibres contain more carbon than stoichiometric SiC would require. In order to characterize the so-called "free carbon" oxygen chemisorption tests were undertaken. It is indeed well known that carbon surfaces are able to chemisorb oxygen after degassing at 1220 K [16, 17]. It is assumed that at 573 K (the chemisorption temperature) the oxidation of SiC can be neglected and will not interfere with the formation of oxygen complexes on carbonaceous species. A sample of SiC powder was taken as a reference in order to confirm this assumption. The oxygen complexes are thermally desorbed as CO_2 and CO upon heating at 1220 K. The amount of CO_2 and CO obtained for desized and HF-treated fibres as well as for the SiC powder are indicated in Table II. Since the samples have different specific surface areas the amounts of desorbed CO_2 and CO have also been calculated per unit surface area. In the case of SiC powder small quantities of CO_2 and CO are desorbed, indicating that even at 573 K oxygen is chemisorbed on a degassed SiC surface. This fact may be attributed to traces of carbonaceous impurities present at the surface and/or to reactive SiC surface sites. It is also seen that the SiC-based fibres chemisorb about ten times more oxygen per unit area than the SiC reference sample. Furthermore it appears that after HF treatment oxygen chemisorption is slightly increased, suggesting an enrichment in carbon of the fibre surface.

During the oxygen chemisorption at 573 K on carbon surface a slight oxidation giving mainly CO_2 also takes place. The respective amounts of CO_2 evolved during oxygen chemisorption for the three samples are indicated in Table III. The comparison of the quantities of CO_2 formed per unit surface area shows that the SiC powder is the less reactive sample, whereas the HF-treated fibre undergoes the highest gasification reaction at 573 K. These results are consistent with the oxygen chemisorption results reported above.

3.3. Oxidation at 973 K

Oxidation treatments were studied at 973 K in a static system with oxygen pressure in the range 70–20 Pa. It was observed that immediately after exposure of the SiC-based fibre to oxygen, evolution of CO and CO_2 started. As an example, oxygen depletion and formation of CO and CO_2 are plotted as a function of time in Fig. 5 for the desized fibre. For longer oxidation time a known quantity of molecular oxygen was reintroduced in the reaction chamber in order to maintain a sufficient oxygen pressure. The formation of CO_2 and CO during long-term oxidation runs of

TABLE II Thermal desorption of carbon monoxide and carbon dioxide from SiC-type materials

Fibre	CO (μmol g^{-1})	CO_2 (μmol g^{-1})	CO + CO_2 (μmol g^{-1})	CO + CO_2/S_{BET} (μmol m^{-2})
Desized fibre	0.43	0.21	0.64	3.0
HF-treated fibre	0.9	0.26	1.16	3.7
SiC powder	1.8	0.19	1.99	0.3

TABLE III Carbon dioxide formation during oxygen chemisorption at 573 K

Fibre	CO_2 (μmol g^{-1})	CO_2/S_{BET} (μmol m^{-2})
Desized fibre	0.1	3.0
HF-treated fibre	0.3	3.7
SiC powder	0.6	0.3

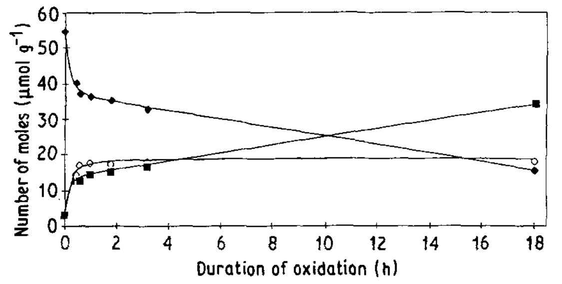

Figure 5 Typical oxidation curve at 973 K: (◆) O_2, (◇) CO_2, (■) CO_2.

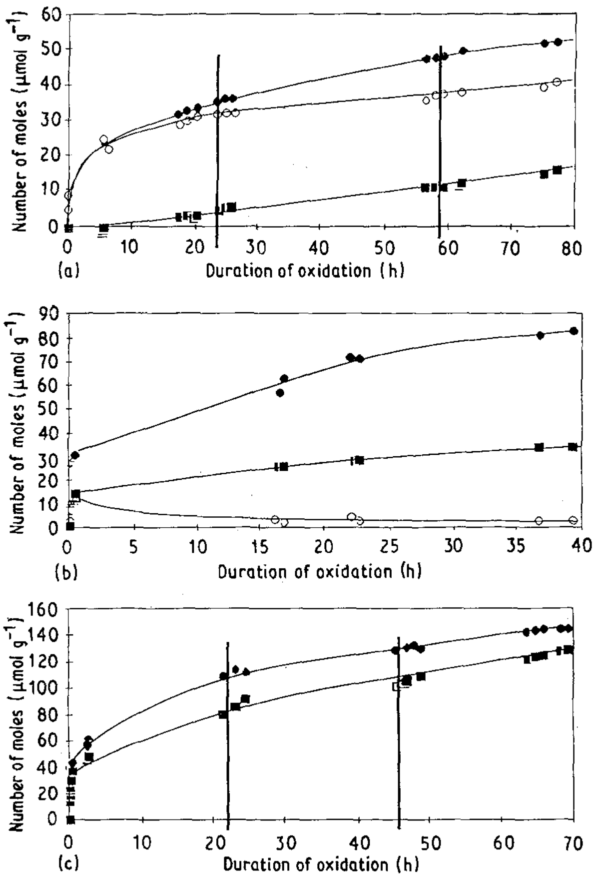

Figure 6 Oxidation curves for (a) desized fibre, (b) desized and HF-treated fibre and (c) SiC reference powder: (◆) CO_2, (◇) CO, (■) O_2 uptake.

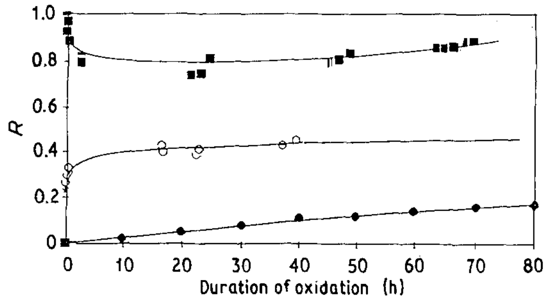

Figure 7 Evolution of the ratio R = (amount of O_2 fixed)/(amount of CO + CO_2 produced) for the different samples versus oxidation duration: (●) desized fibre, (○) HF-treated fibre, (■) SiC powder.

desized fibres, HF-treated filaments and SiC powder are shown in Fig. 6a, b, and c, respectively. Vertical lines indicate the time at which oxygen was reintroduced in the reaction chamber. It is seen that reintroduction of oxygen does not significantly affect the overall oxidation reaction of the samples. In the case of desized fibres CO_2 and CO are formed, whereas for the HF-treated fibre only a small quantity of CO appears at the beginning of the reaction and thereafter disappears, probably by conversion into CO_2. For SiC powder only CO_2 is formed.

The amount of oxygen fixed on the fibre at time t, $n(O_2)_{ads}$, can be determined from the oxygen balance according to the following equation:

$$n(O_2)_{ads} = n(O_2)_{init} - (nO_2 + nCO_2 + 0.5nCO)$$

where $n(O_2)_{init}$ is the initial amount of oxygen and nO_2, nCO_2, nCO are the respective amounts of O_2, CO_2 and CO present in the gas phase at time t. The oxygen uptake of the various samples during oxidation is also shown in Fig. 6. It is seen that for all samples the uptake of oxygen increases with oxidation time. There are, however, some differences in the kinetics of oxygen uptake. For the SiC powder and the HF-treated fibre, a significant amount of oxygen is fixed at the beginning of the reaction. For the desized fibre, a detectable uptake of oxygen takes place only after 10 h of reaction.

4. Discussion

The formation of hydrogen above 1100 K clearly indicates that an organic character is still present in the fibre. The amount of hydrogen desorbed at 1370 K is much higher than the quantity of CO and CO_2 formed in the same conditions (see Table I). This observation and the subsequent H_2 evolution at 1470 K suggest that the gas is not formed only in the outer layers but also originates from chemical reaction affecting the bulk of the fibre. In contrast the amount of carbon gasified as CO and CO_2 is sufficiently small to be formed only in the surface layers (2.6 μmol g^{-1}). Considering the surface area of the desized fibre, the amount of carbon desorbed as CO and CO_2 would be equal to 7.8 molecules per nm^2. Upon repeated oxygen chemisorption and TPD cycles an even smaller amount of carbon is gasified (0.6 μmol g^{-1}). Assuming, as for graphitized carbons, that the area of an oxygen chemisorption site is equal to 0.083 nm^2 [16], the surface density of carbon active sites would represent about 20% of the total surface area for the desized fibre. This result clearly indicates that the surface of the SiC-based fibres contains a significant amount of sites which behave like free carbon.

The presence of free carbon species can also be evidenced from the oxidation studies. At 970 K a carbon material reacts with oxygen and give rise essentially to CO and CO_2. In the same conditions the oxidation of SiC leads to the fixation of oxygen on the solid and to a gasification of carbon according to the following reactions:

$$SiC + 2O_2 \rightarrow SiO_2 + CO_2 \qquad (1)$$

$$SiC + \tfrac{3}{2}O_2 \rightarrow SiO_2 + CO \qquad (2)$$

Defining R as the ratio of the number of moles of O_2 fixed on the solid to the number of moles of C gasified at time t, one obtains an estimation of the fraction of carbon monoxide or dioxide originating from SiC or from free carbon. In fact R is equal to 0 and 1 for carbon and SiC, respectively. The values of R for the different samples have been determined after various exposure times to oxygen (Fig. 7). It is seen that for SiC powder, R is comprised between 0.8 and 1 during the whole period of oxidation. According to Reactions 1 and 2, the theoretical value of R should be equal to 1. Actually R is systematically smaller than 1. Hence after 80 h of oxidation R is equal to 0.86 and experimental uncertainities cannot explain this difference. Nevertheless, the value of R for SiC powder is much closer to unity than for the SiC-based fibres.

Considering the desized fibre, R is close to zero during the first 10 h of oxidation and thereafter increases steadily. This result suggests that at the beginning the evolution of CO and CO_2 essentially comes from the oxidation of a "free" carbon-type material. From a kinetical point of view, it is seen that about 20 μmol of carbon per g are instantaneously gasified, indicating a high reactivity as well as proper accessibility of the carbon to oxygen.

Afterwards, the oxidation rate decreases significantly. For instance, the average oxidation for the first 5 h of oxidation, i.e. when no oxygen uptake on the fibre takes place, is equal to 9 μmol $g^{-1} h^{-1}$. In the same conditions, the oxidation rate of a carbon fibre can be estimated to 10000 μmol $g^{-1} h^{-1}$ [17].

As R keeps a very low value (small contribution of SiC oxidation compared to the fibre treated with HF), it may be concluded that the free carbon aggregates are associated with a silica-type layer which considerably restricts its oxidation rate. For oxidation times above 10 h, R increases: oxygen diffuses through the silica surface layer and reacts with SiC-type structure lying beneath. The oxidation proceeds then on an increasing fraction of SiC-type structure and free carbon structure as well.

Treatment of the SiC-based fibre with HF prior to oxidation has a striking effect on its reactivity. At first the value of R is considerably higher as for the untreated HF fibre indicating a significant contribution of SiC structure to the overall oxidation process. At the beginning of oxidation ($T < 2$ h), R increases from 0.22 to 0.35 and thereafter remains more or less close to 0.44.

An increase of R at the beginning of reaction suggests a preferential removal of free carbon. Afterwards SiC oxidation and free carbon gasification proceeds in an almost constant proportion. Although the precise molecular structure of the SiC-based fibres is not known yet, it has been reported that it consists approximatively of 49% SiC, 40% free carbon and 12% SiO_2 on a molar basis [15]. Considering these data and assuming that SiC and C are oxidized at the same rate (diffusion-controlled kinetics), a theoretical value of R equal to 0.55 can be obtained. This value has to be compared with the one found experimentally with the HF-treated fibre ($R = 0.44$). It appears that these two values compare reasonably well if one considers the experimental uncertainity as well as the oversimplified molecular structure from which R has been theoretically calculated. Hence it may be concluded that after removal of the silica layer by HF, the oxidation behaviour strongly suggests the presence of SiC structure and fine carbon aggregates in the SiC-based fibre.

5. Conclusion

The chemical behaviour of the fibres studied and of the SiC powder in neutral and oxidizing environments clearly shows the complex structure of the Nicalon NML 202 fibre: it is a ceramic fibre in spite of an organic character remaining from the precursors. Beneath a silica-rich sheath, the bulk contains free carbon associated with a silicon carbide-based network.

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