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Thermal stability of SiC fibres (Nicalon®)

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The degradation behaviour of Nippon Carbon Co. SiC fibres (Nicalon®) after heat treatment in various environments was studied. Regardless of the heat-treatment conditions, the Nicalon® fibre strength degraded when the fibres were subjected to temperatures higher than 1200° C (temperatures below 1200° C were not investigated). This degradation is associated with the evaporation of CO from the fibres as well as with β-SiC grain growth in the fibres.

1. Introduction

Recently, ceramic composites, especially ceramic fibre-reinforced composities, have become increasingly attractive for high-temperature structural applications. The current commercial availability [1–8] of continuous fine-grained polycrystalline SiC fibres (Nicalon®) has facilitated the development of high-strength and high-fracture-toughness ceramic composites [9–11]. However, the thermal instability of these ceramic composites in temperature regimes of ~ 1000° C and above, which is often the result of fibre–matrix interfacial degradation, has prevented the prolonged application of these composites at higher temperature.

The present investigation was carried out to study the degradation behaviour of fibres under various heat-treatment temperatures and environments and subsequently to make tensile-strength measurements on these fibres. The fibre degradation was analysed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), secondary-ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), and X-ray diffraction (XRD).

2. Characterization procedures

SiC fibres produced by Nippon Carbon Co. (Nicalon®) were procured for this study in the form of yarn with ~ 500 fibres per tow, the average fibre diameter being 13 μm. The average length of the tow was ~ 800 m, and the density was reported by the vendor to be 2.55 g cm^{-3}. Vinyl acetate was used as a sizing resin.

2.1. Heat treatments

The fibre heat treatments were performed at three temperatures (1200, 1300 and 1400° C) in three environments (argon, 5×10^{-5} torr vacuum, and air). Heat treatments in argon and vacuum were conducted in a Brew® furnace equipped with a tungsten-mesh heating element, and heat treatment in air was carried out in a furnace equipped with a super-Kanthal® ($MoSi_2$) resistance heating element. The desired heat-treatment temperatures were reached within 45 min; and after a 2 h soaking the fibres were furnace cooled.

2.2. Tensile tests

The tensile strength and Young's modulus of the fibres were measured on a universal testing machine equipped with pneumatic grips. Measurements were made at a crosshead speed of 0.508 mm min^{-1} (0.02 in min^{-1}). Specimen load was sensed by a 500 g capacity Instron Type-A load cell. This cell was mechanically calibrated by precision standard weights prior to testing each set of fibre specimens. A calibration check was also performed at the conclusion of each test set. A load against

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TABLE I Summary of tensile test results

Fibre treatment	Number of tests	Tensile strength [MPa (10^3 psi)]	Young's modulus [GPa (10^6 psi)]
As received	10	1765 (256)	106 (15.4)
Sizing removed with acetone	14	2110 (306)	118 (17.1)
1200° C in argon	13	1234 (179)	180 (15.6)
1300° C in argon	13	1262 (183)	110 (15.9)
1400° C in argon	15	848 (123)	104 (15.1)
1200° C in vacuum	5	345 (50)	94 (13.6)
1300° C in vacuum	10	200 (29)	47.6 (6.9)*
1200° C in air	15	660 (95.7)	110 (16.0)
1300° C in air	12	1262 (183)	114 (16.6)
1400° C in air	13	1379 (200)	102 (14.8)

Note that tests on fibres heat treated in vacuum at 1400° C could not be performed due to the extreme brittleness of the specimen.

* Due to low failure loads, significant error may have been introduced in the extension measurement. Load–deflection curves have a minimal linear portion.

crosshead displacement curve recorded by the testing machine was used to determine fibre-specimen failure load and extension.

The fibre-mounting technique employed Kodak 2 x 2 in. 35 mm slide mounts as supports for the individual test fibres. The slide mounts were prepared to receive the test fibres by first punching precisely located holes in the card to enable the card to be mounted in a specially designed fixture which produced a fibre-alignment groove. The alignment groove makes possible the mounting of test fibres perpendicular to and centred with respect to the card.

Fibre specimen mounting was completed by placing a single fibre in the card-alignment groove and fastening the fibre ends with jeweller's wax. After a fibre specimen had been mounted to a card, a narrow section of the card was cut away in a hole-punching fixture. Paper binding clips were placed on the cut card to maintain fibre alignment until the assembly could be positioned in the testing machine. When the fibre test specimen had been secured in the tensile grips of the testing machine, the binder clips were carefully removed and the fibre loaded to failure. The tested fibre mounts were examined to determine test validity, and only those specimens which had not failed at the wax supports were accepted. The diameter of each valid test specimen was measured under the optical microscope with a filar micrometer.

2.3. Analysis

SEM analysis was performed on SiC fibres from each set of heat treatments as well as on fibres as-recieved. SiC fibres from a selected set of heat-treatment conditions were also examined in the TEM. These fibres were impregnated with resin and microtomed with a diamond blade. The thin sections were then placed on copper grids and examined in the TEM. As-received and heat-treated fibres were also ground into powder form and standard powder XRD analyses carried out. To a limited extent, fibre out-gassing studies were performed utilizing SIMS. Selected fibre samples were also analysed by means of a small-spot-size scanning Auger microprobe.

3. Results and discussion

Table I is a summary of the tensile-test results for SiC fibres subjected to various heat treatments. The average tensile strength (2110 MPa) of the fibres after sizing removal is very close to the value ($\cong$ 2500 MPa) reported by the supplier. However, the Young's modulus (118 GPa) is considerably lower than the reported value (180 GPa). The strength-data spread within the set of test values was sufficiently small to make a valid comparison possible. The modulus measurements used in this study relied on the coupling between chart recorder and crosshead movements for the measurement of strain; hence, a considerable error could be present. The values of Young's modulus reported here should be considered tentative; however, the variations in modulus between the different heat treatments should be real.

3.1. Argon heat treatment

Fibres showed considerable degradation upon heat

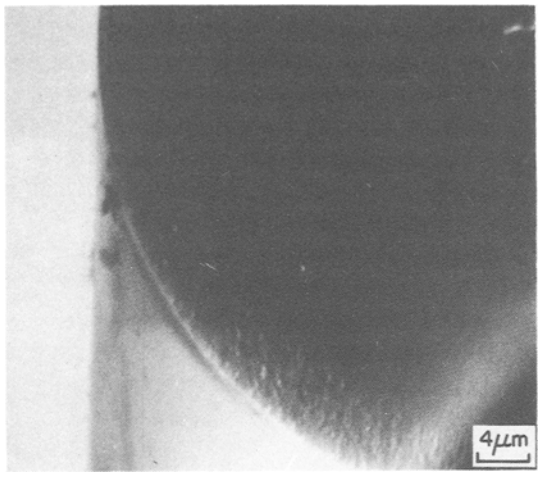

Figure 1 Nicalon® fibre heat treated for 2 h in static argon (100 μm Hg) at 1400° C.

treatment in argon. After 1200° C heat treatment, the strength dropped to about half the original value. After 1300° C heat treatment, the strength reduction was the same as for the 1200° C heat treatment; after 1400° C heat treatment, a more severe strength degradation was observed.

SEM fractographs of 1200° C and 1300° C argon heat-treated fibres show a featureless structure which resembles the fracture surface of fibre glass. However, after 1400° C heat treatment, the fibre fracture surface exhibits a reaction zone in the periphery of the fibre (Fig. 1). This behaviour is shown more clearly in the transmission electron micrographs and their corresponding electron-diffraction ring patterns (Fig. 2). The as-received fibre exhibits a very diffuse, broad ring pattern which may be thought of as originating from "amorphous" solids, whereas the fibres may actually be crystalline β-SiC – but only a few unit cells in grain size. The 1400° C argon heat-treated fibre shows a coarsening of β-SiC in the outer layer and a less-diffuse diffraction ring than in the as-received state; however, the grain size is still very small.

3.2. Vacuum heat treatment

The tensile-strength degradation of Nicalon® fibres after vacuum heat treatment is rather extreme. The fibres heat treated at 1400° C in vacuum could not be tested owing to extreme brittleness and fragility. SEM fractographs of the 1200° C vacuum heat-treated fibre show that the degradation reaction initiated from the surface of the fibre and proceeded toward the centre (Fig. 3). The degradation zone appears to be associated with grain growth. The 1300° C vacuum heat-treated fibre shows that degradation has taken place throughout the fibre. However, the inner core of the fibres having large diameters did not degrade; this result further supports degradation-reaction initiation from the surface of the fibre. At 1400° C further degradation has occurred inside the fibre, and a thick layer has formed at the outer surface of the fibre (Fig. 4).

TEM observations on the 1200° C vacuum heat-treated fibre reveal (Fig. 5) a very interesting feature, i.e. coarse and reasonably well developed β-SiC grains at the periphery of the fibre and a gradual decrease in grain size toward the centre of the fibre. This observation is well correlated with the SEM micrograph (Fig. 3). The corresponding SAD pattern shows the inner portion of the fibre to be very similar to that of the as-received fibre. The outer section of the fibre shows a spotty ring pattern which implies reasonably well-developed β-SiC crystals. The bright-field images and SAD ring pattern of the 1300° C and 1400° C vacuum heat-treated fibres are shown in Fig. 6. The 1400° C heat-treated fibres contain somewhat larger (~ 50 nm) grains than the 1300° C heat-treated fibre, and the diffraction ring patterns of both are those of a well-developed fine-grained β-SiC.

3.3. Air heat treatment

The tensile strengths of fibres heat treated in air show a reverse trend to that of the argon or vacuum heat-treated fibres. After 1200° C heat treatment, the strength dropped to about one-third the as-received value but increased (or maintained a large portion of the original strength) after 1300 and 1400° C heat treatments. The SEM micrographs show the formation of an SiO_2 film (based on XRD and TEM) on the surface and a thickness increase with increasing heat-treatment temperature. A severe example of 1400° C air heat-treated fibres is shown in Fig. 7. These fibres were air heat treated in an SiC resistance furnace, and the heating rate was much slower than that of the $MoSi_2$ heating-element furnace where fibres were heat treated for tensile-strength measurements. In the latter case, the SiO_2 film was much thinner. TEM (SAD) observations on the fibres heat treated in air show a distinct α-cristobalite diffraction pattern in the oxidized region. The inner regions of the fibre resemble those of the argon heat-treated fibres.

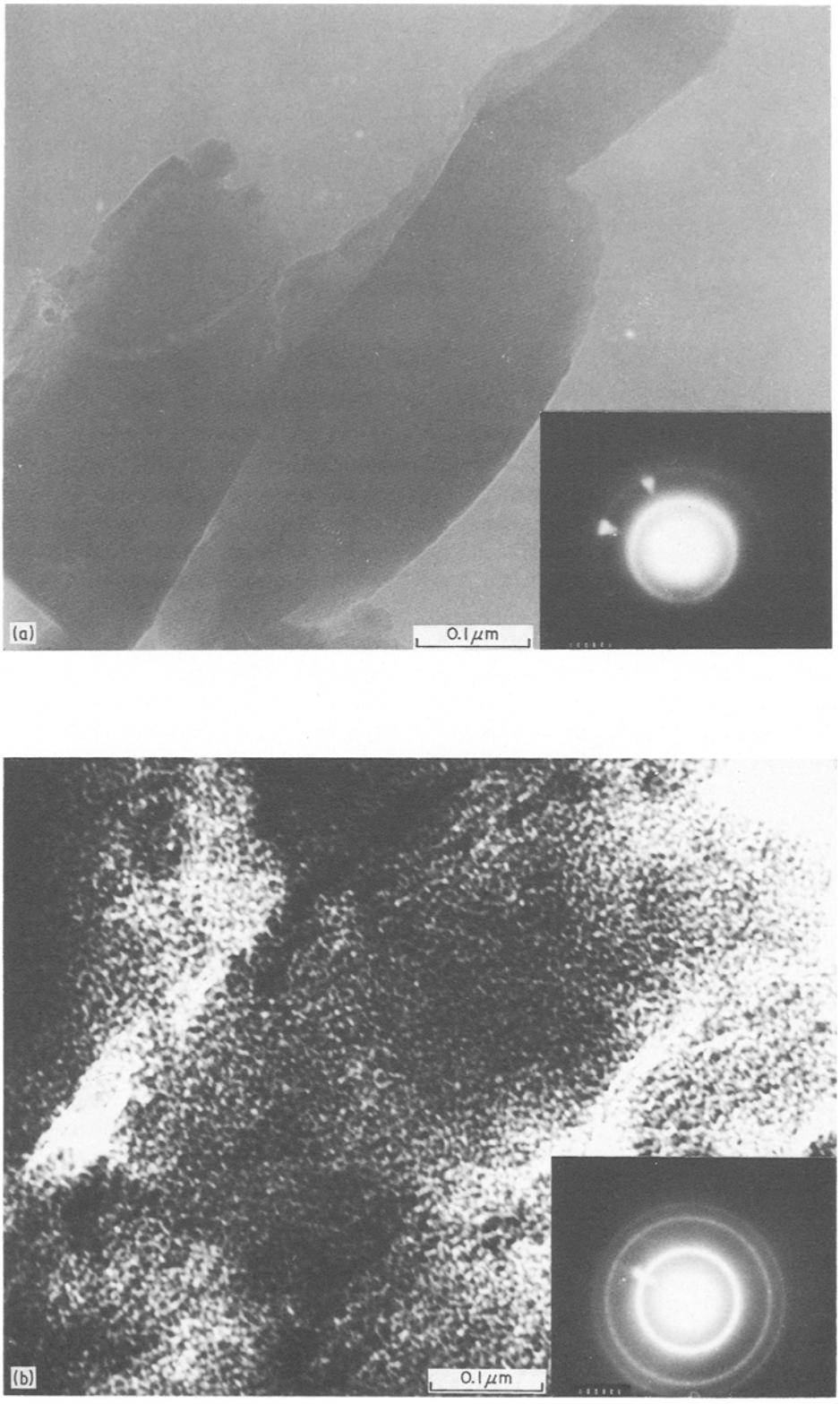

Figure 2 Bright-field images and ring patterns for Nicalon® fibres. (a) as-received, (b) heat treated for 2 h in argon at 1400° C.

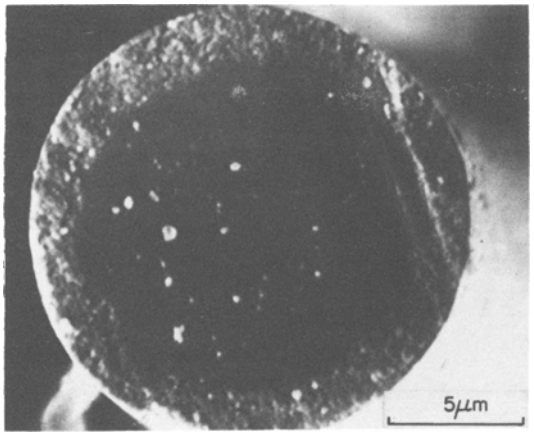

Figure 3 Nicalon® fibres heat treated for 2 h in vaccum (5×10^{-5} torr) at 1200° C.

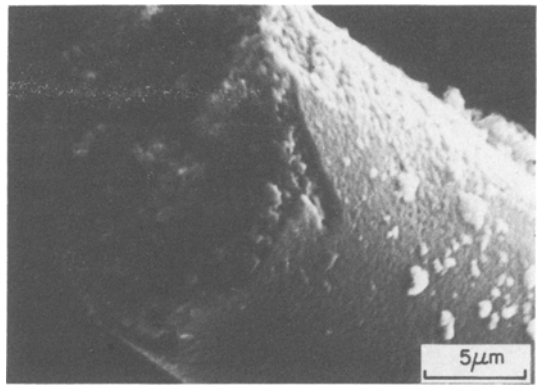

Figure 4 Nicalon® fibres heat treated for 2 h in vacuum (5×10^{-5} torr) at 1400° C.

3.4. XRD analysis

Powder XRD analyses were conducted in order to observe the development of β-SiC as well as to analyse the particle size by the line-broadening technique. Typical examples of XRD patterns of β-SiC (111) diffraction are shown in Fig. 8. The β-SiC particle size of the as-received fibre was calculated to be 1.6 nm, and that of the 1400° C-argon-heat-treated fibre was 5.1 nm. In the case of the 1200° C-vacuum-heat-treated fibres, the particle size was calculated to be 8.0 nm; however, the XRD pattern shows overlapping peaks – a broad peak with a sharp peak at its middle. This observation correlates well with the SEM micrograph where the coarse and well-developed SiC grains at the fibre periphery yield a sharp peak in the XRD pattern, and the middle portion of fibre is responsible for the broad XRD peak. The XRD patterns of the 1300° C and 1400° C vacuum heat-treated fibres are similar to a very well developed SiC powder-diffraction pattern.

The XRD analyses on the fibres heat treated in air show β-SiC as well as α-cristobalite peaks. The SiC particle-size measurement of air heat-treated fibres based upon the line-broadening technique revealed a value comparable to that of the argon heat-treated fibres.

3.5. Secondary ion mass spectrometry (SIMS)

On the basis of the above-described observations, it is expected that a series of degradation processes is occurring during heat treatment. The most noteworthy events are reaction-dissociation, oxidation, and grain growth. It is reported [8] that the atomic ratio of SiC fibres after pyrolysis (1300° C) of the precursor fibre is Si:C:O:H = 1:1.46:0.36:0.03. This as-received fibre composition thus contains a considerable amount of excess carbon and oxygen. In order to study the fibre out-gassing behaviour, a small furnace was constructed and inserted into the SIMS. The furnace built for these studies consisted of a tungsten heating element wound into a coil about 3 mm in diameter and 2.5 cm long and encased in a stainless-steel tube. Nicalon® fibres were placed in the tungsten coil, and the unit was inserted into the SIMS vacuum chamber. As the tube was heated, the gases evolved were identified using the mass spectrometer. The fibres were heated to temperatures in excess of 1300° C.

At low temperatures (600° C), the typical surface contaminants are evolved. At elevated temperatures, carbon monoxide is evolved from the fibre samples. The spectrograph for the out-gassing species recorded at 1200° C is shown in Fig. 9. SEM micrographs of the surface of the fibres analysed at 600° C showed no surface deterioration; however, the 1200° C samples showed the beginnings of the surface pitting, and the 1300° C samples showed considerable pitting on the fibre surface.

3.6. AES analysis

As-received fibres as well as 1200° C-vacuum-heat-treated fibres were examined using the small-spot-size JEOL JAMP-105 scanning Auger microprobe. Fig. 10 is an Auger spectrum taken at the centre of a fractured fibre as-received. This surface was ion etched *in situ* to remove any con-

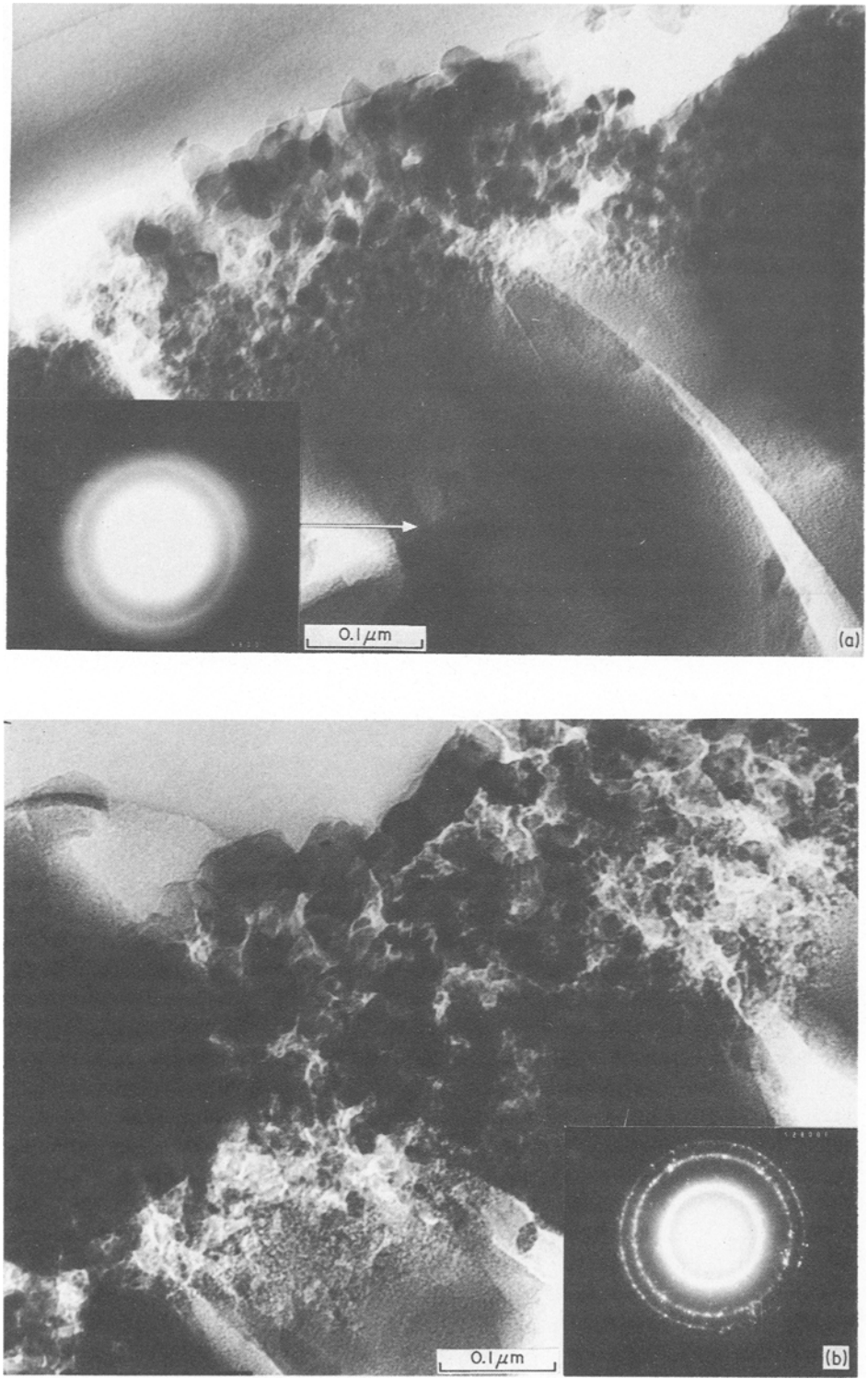

Figure 5 Bright-field images and ring patterns from Nicalon® fibres heat treated for 2 h in vacuum at 1200° C, (a) outside coarse grain and (b) inside fine grain.

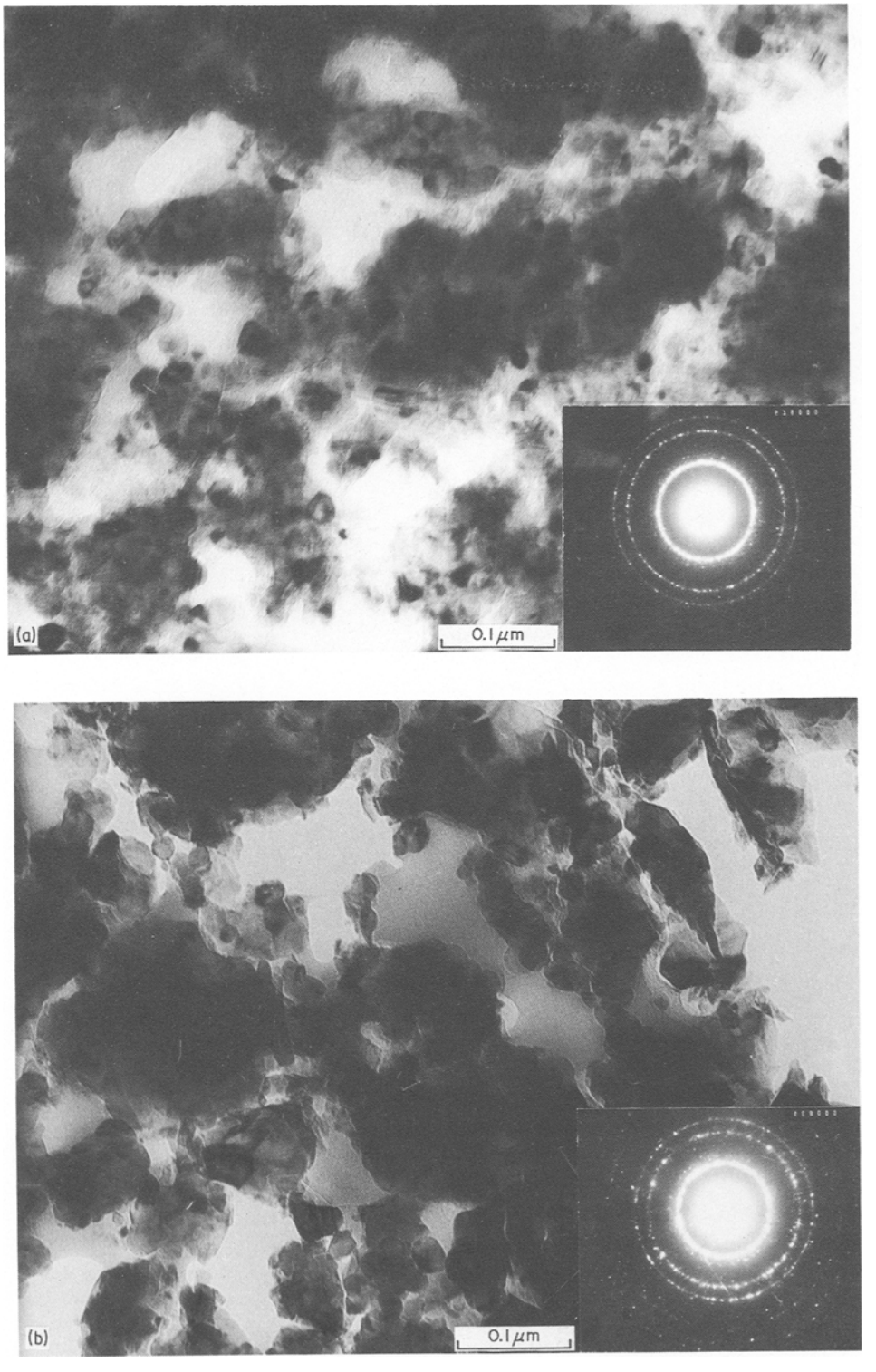

Figure 6 Bright-field images and ring patterns from Nicalon® fibres heat treated for 2 h in vacuum at (a) 1300° C and (b) 1400° C.

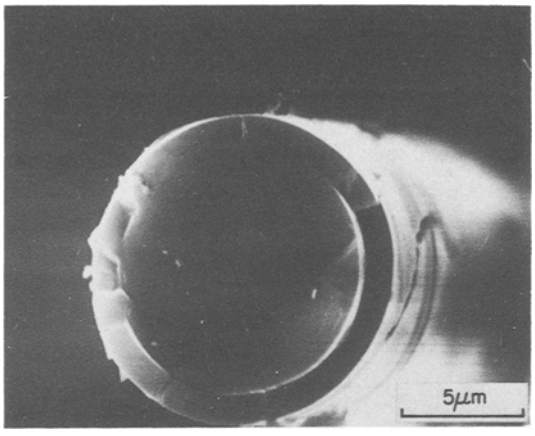

Figure 7 Nicalon® Fibre heat treated for 2 h in air at 1400° C.

taminants which may have resulted from atmospheric exposure. On the basis of this spectrum, the fibre contains oxygen and nitrogen throughout. The carbon-peak shape indicates that Si–C type bonding is not apparent; in fact, C–C, C–H, and C–O type bonding are all possible. It is difficult to say whether Si–C bonding is completely absent; if it is present, it is obscured by other, more abundant forms of carbon bonding. The Auger spectra taken at the centre and outside reaction zone of 1200° C vacuum heat-treated fibre (Fig. 3) are shown in Figs. 11 and 12, respectively. The former is quite similar to that of the as-received fibre, and the latter shows that nitrogen has been depleted and the oxygen level has been reduced. The carbon-peak shape shows the presence of Si–C bonding.

The strength degradation of fibres after heat treatment can be explained as follows. At 1200° C, excess carbon present in the fibre reacts with oxygen and escapes from the fibre. The degree of evolution of CO gas would be much greater in vacuum than in argon or air. The evolution of CO from the fibre leaves behind a hole in the fibre, and this is an on-going process. As a result, the fibre strength is degraded from the as-received state due to deep notches in the fibre. The depth of the notch is expected to be much greater in vacuum than in air or argon; hence, the largest strength reductions are observed in the vacuum heat-treated fibres. The lower strength after heat treatment in air as compared to argon at 1200° C is due to the greater availability of oxygen in air. This causes deeper notches to be formed on the fibres. At this temperature a protective SiO_2 surface layer is not well developed in air, and the reacted CO escapes freely from the fibre. For heat treatment in air at

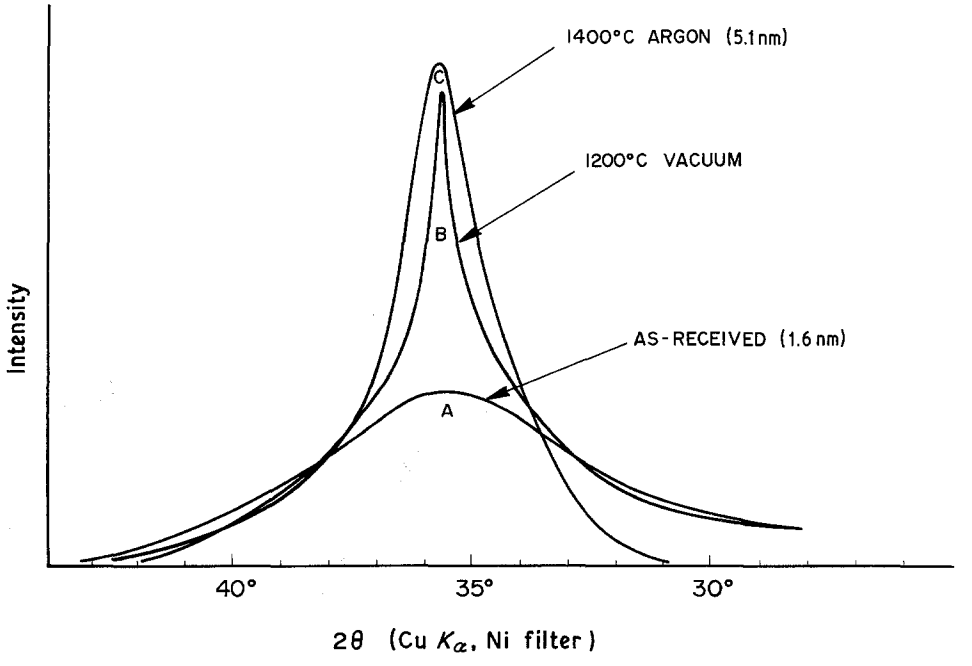

Figure 8 XRD pattern of β-SiC (1 1 1) diffraction for three conditions: (a) as-received, (b) 1200° C, 2 h in vacuum and (c) 1400° C, 2 h in argon.

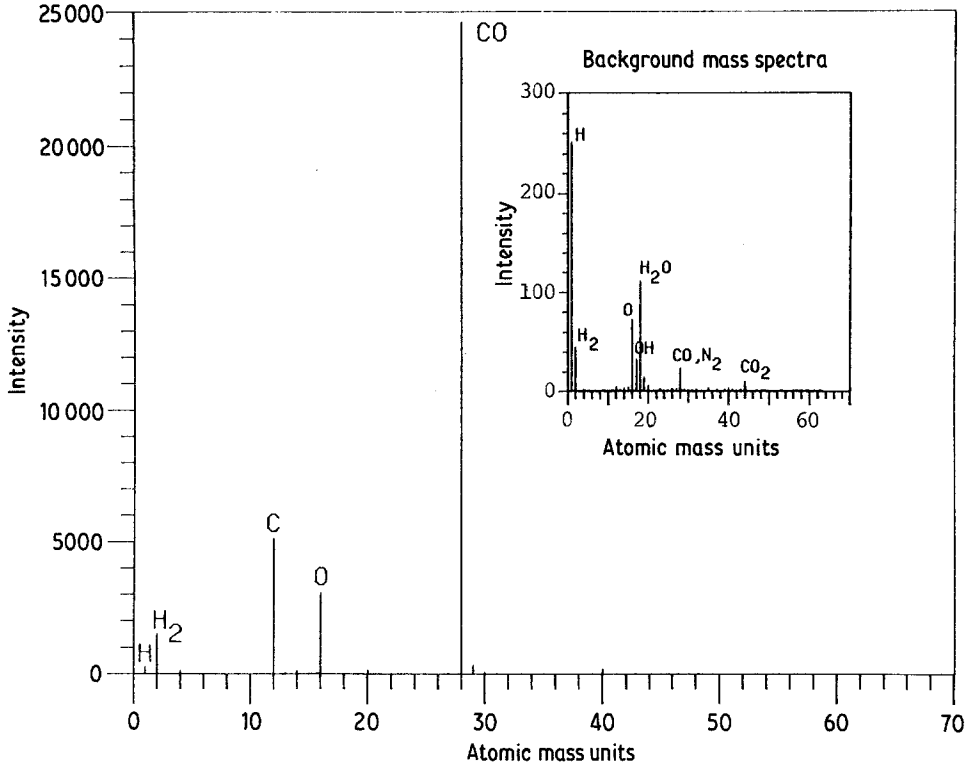

Figure 9 CO mass spectra for Nicalon® fibres at 1200° C in vacuum.

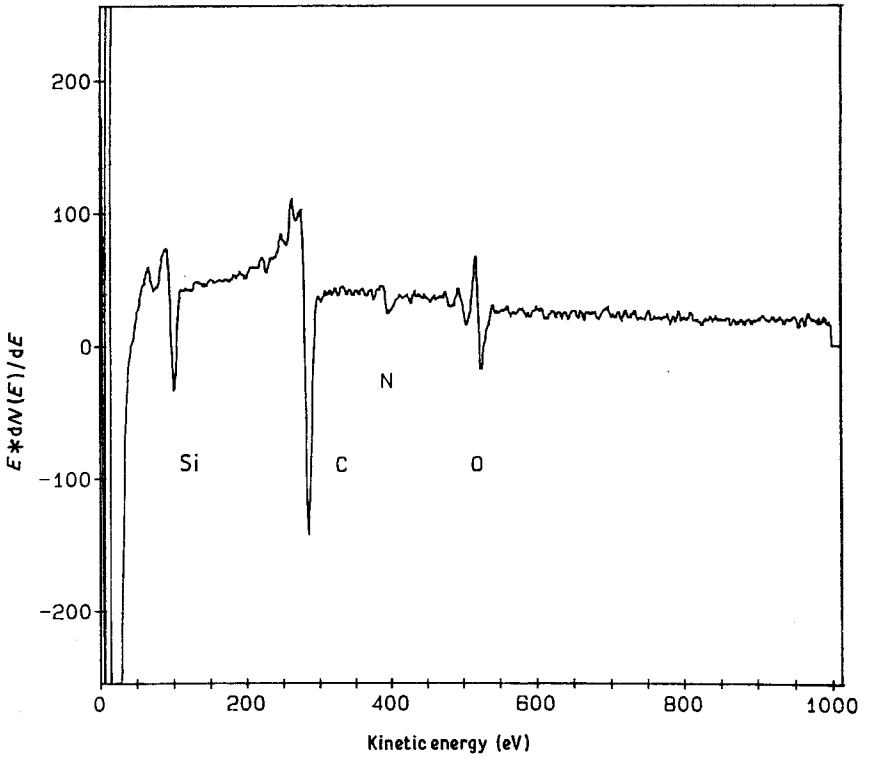

Figure 10 Auger spectrum taken at the center of a fractured as-received fibre.

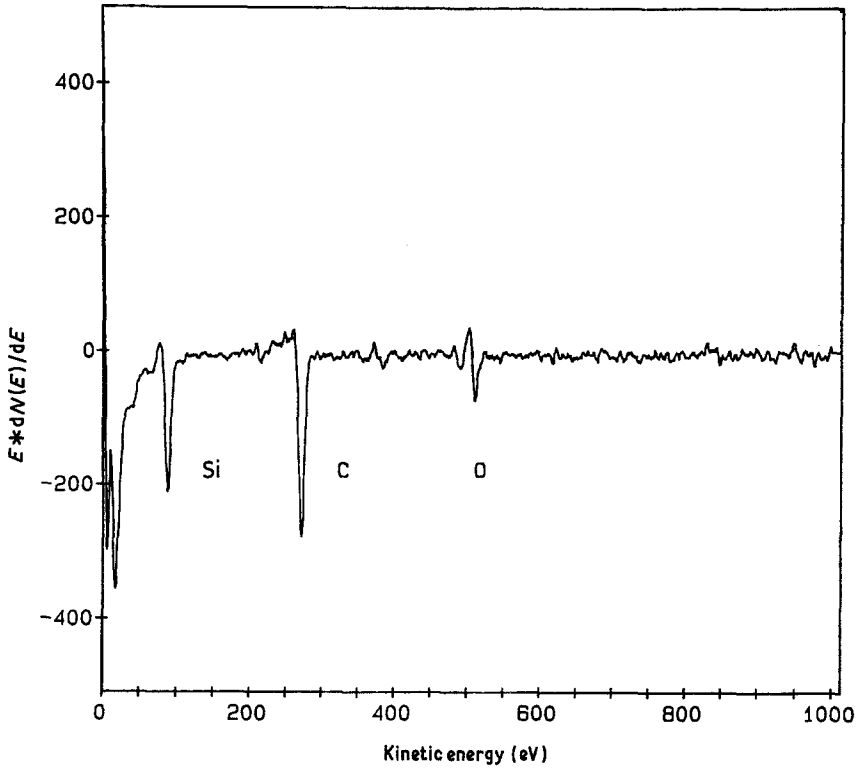

Figure 11 Auger spectrum taken from the centre of the 1200° C vacuum heat-treated fibre.

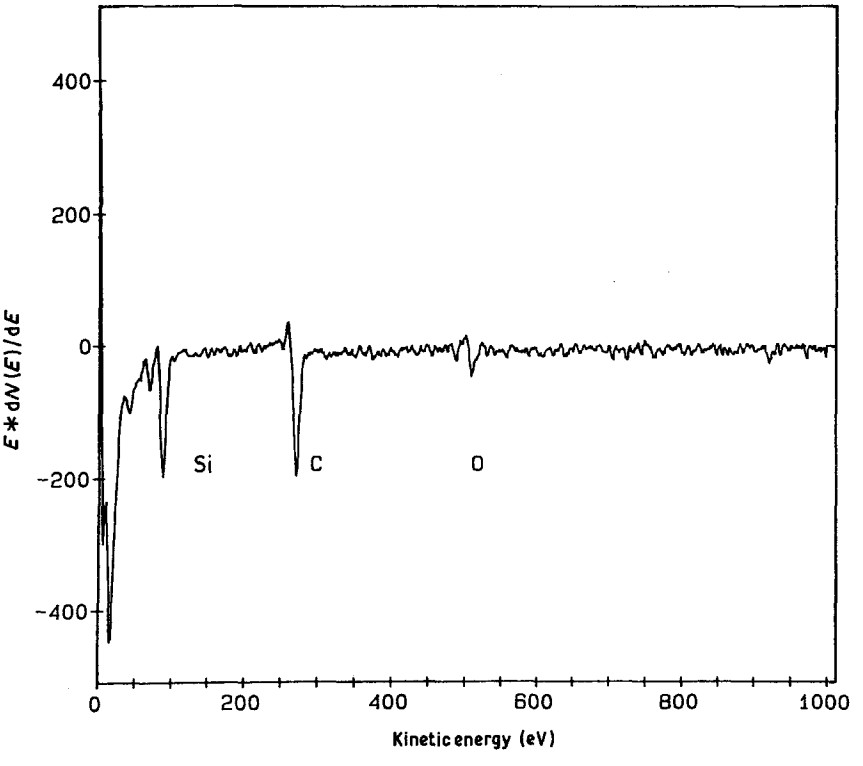

Figure 12 Auger spectrum taken from the reacted region of the 1200° C vacuum heat-treated fibre.

1300° C, the protective SiO_2 surface layer builds up more than at 1200° C and thus suppresses CO evolution in the fibre. At 1400° C, the protective surface layer is well developed, with an attendant increase in strength (or maintenance of a large portion of the as-received strength).

4. Conclusions

The tensile strengths of Nicalon® fibres after high-temperature heat-treatment depend not only upon temperature but also upon heat-treament environment. Regardless of the heat-treatment conditions, the Nicalon® fibre strength degraded when the fibres were subjected to temperatures higher than 1200° C (temperatures below 1200° C were not investigated). This degradation is associated with the evaporation of CO as well as with β-SiC grain growth. The mechanism of grain growth is not clear at present; however, it appears to be associated with the evaporation of excess carbon (as CO) from the fibre. The thermal stability of Nicalon® fibres in a composite, however, may be entirely different from the case of bare fibre exposure, and this area holds great promise for further research.

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