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High-temperature stability of Nicalon under Ar or O_2 atmosphere

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The thermal stability of Nicalon NL400 at 1573, 1673 and 1773 K has been studied by TGA and XRD. Under an Ar atmosphere, Nicalon pyrolysed severely to crystallize into β-SiC involving the generation of both SiO and CO. Under an O_2 atmosphere, the oxide film which formed around Nicalon retarded the pyrolytic reaction of the core. Nicalon coated with a silica film by the previous oxidation treatment pyrolysed hardly at all under an Ar atmosphere, because the film restricted the escape of SiO and CO. Nicalon which was oxidation-treated at 1773 K retained 63% of its original strength after heating at 1773 K under an Ar atmosphere. The amorphous silica film was found to resist rapid thermal cycling between room temperature and elevated temperatures.

1. Introduction

Amorphous Si–C–O fibre, manufactured on an industrial scale with the trade name Nicalon by Nippon Carbon Co., is attractive as a reinforcing fibre in ceramic-matrix composites [1, 2]. Nicalon is prepared by firing thermal oxidation-cured polycarbosilane fibre and is regraded as an intermediate product before transformation into β-SiC, i.e. it is thermodynamically metastable. Therefore, when Nicalon is heated at higher temperatures, crystallization to β-SiC occurs and both SiO and CO gases are generated [3–5]. As a result of this pyrolysis, the tensile strength of Nicalon decreases markedly [6–8].

There are two approaches to the suppression of the pyrolysis. The first approach is reduction of the oxygen content as a driving force of the pyrolysis, in order to make the fibre more thermodynamically stable. Recently, fibre with a low oxygen content has been prepared using the radiation-curing method [9, 10]. The second approach is suppression of the evolution of SiO and CO by the coating of Nicalon. Both CVD–SiC and oxide film have been proposed to be effective as the coating layer [11–15]. In particular, Nicalon coated with an oxide film can be prepared readily and cheaply using simple apparatus.

In the present work the chemical stability of Nicalon NL400, the pyrolysis of which occurs faster than that of NL200 [4, 5], was investigated in an Ar or an O_2 atmosphere at temperatures between 1573 and 1773 K. The pyrolysis of Nicalon coated with an oxide film was then investigated under thermal cycling conditions of rapid cooling and heating from room temperature to 1773 K. The results of these experiments are discussed in relation to the mechanism of pyrolysis.

2. Experimental procedure

Three types of experiment were carried out as follows:

(i) pyrolysis of Nicalon,
(ii) oxidation of Nicalon,
(iii) pyrolysis of Nicalon coated with oxide film.

Nicalon used in experiments (i) and (ii) was heated in Ar at 1073 K for removal of the sizing agent prior to measurement. The fibres used in experiment (iii) were oxidized (mass gain of $100\Delta W/W_0 = 1.4$) in an O_2 atmosphere at 1573 K for 21.6 ks or 1773 K for 10.8 ks, and then cooled rapidly to room temperature. W_0 and ΔW are the initial mass of Nicalon and the mass change measured with a thermobalance, respectively. Nicalon samples oxidized at 1573 and 1773 K are named "fibre-a" and "fibre-b", respectively. The thickness of the oxide film is calculated as $b = 4.71 \times 10^{-1}$ μm from the following equations:

$$X = \frac{\Delta W}{W_0} \Bigg/ \left(\frac{M_{SiO_2} - (M_{Si} + 1.21M_c + 0.40M_O)}{M_{Si} + 1.21M_c + 0.40M_O} \right) \quad (1)$$

$$b = d_0[1 - (1 - X)^{1/2}] \quad (2)$$

where X is the oxidation degree of Nicalon, d_0 the initial diameter of Nicalon and M_i the molecular weight of component i. Equation 1 is derived from the stoichiometry of Reaction 4 below.

The thermobalance unit used for thermogravimetric analysis (TGA) was composed of an analogue-type automatic recording balance and an SiC resistance furnace. The experimental temperature was measured with a Pt/Pt–13% Rh thermocouple positioned close to the sample. When the desired temperature was reached, either Ar or O_2 was allowed to flow from the

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bottom of the furnace at $8.8 \times 10^{-6}\ \mathrm{m^3\,s^{-1}}$. Fibres 1 g in mass and 3 cm in length were placed in a magnesia crucible of 26 mm inner diameter and 35 mm depth. The magnesia crucible was suspended in the hot zone of a furnace (alumina reaction tube of 44 mm inner diameter) with an alumina rod and a platinum wire to the balance. The mass change was recorded automatically during each experiment. Upon completion of the TGA measurement the fibres were cooled rapidly by raising the crucible to the low-temperature zone of the furnace. The reaction products were examined by X-ray diffraction (XRD) and by scanning electron microscopic (SEM) observation.

For the fibres with which experiment (iii) was done, the tensile strength was measured in the following way. The oxide layer was first removed with NH_4F + HF solution. Using a load cell of 100 g, tensile testing of a monofilament of 10 mm gauge length was carried out on a Tensilon-type machine (Toyo Measuring Instrument Co. Type UTM-II-20) at a crosshead speed of $2\ \mathrm{mm\,min^{-1}}$.

3. Results

3.1. TGA curves

Fig. 1 shows TGA curves of Nicalon heated isothermally at 1573, 1673 and 1773 K under an Ar atmosphere. The mass loss observed is due to the occurrence of the following pyrolytic reaction:

$$\mathrm{SiC_{1.21}O_{0.40}(s) = 0.905SiC(s) + 0.095SiO(g) + 0.305CO(g)} \qquad (3)$$

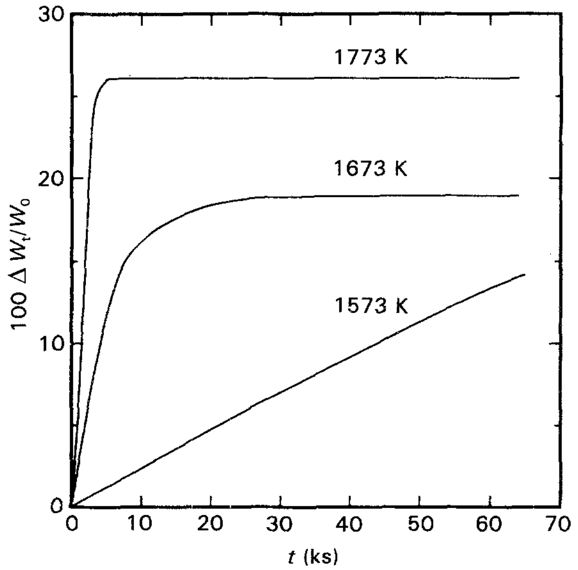

Figure 1 Mass loss of Nicalon heated in Ar at 1573, 1673 and 1773 K.

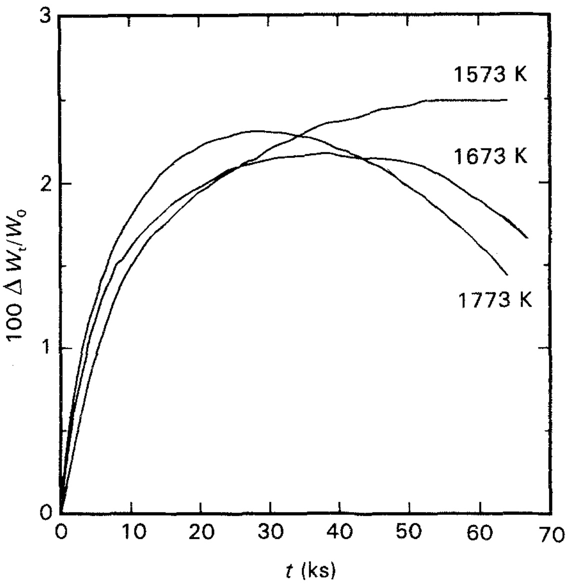

Figure 2 Mass gain of Nicalon heated in O_2 at 1573, 1673 and 1773 K.

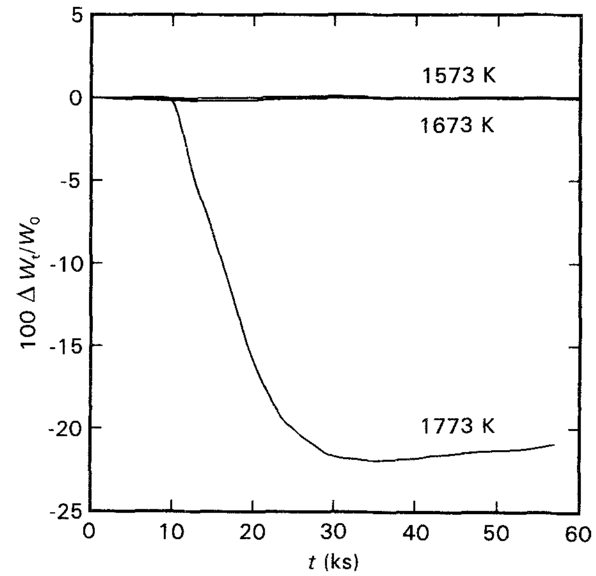

Figure 3 Mass change of fibre-a (Nicalon oxidation-treated at 1573 K) heated in Ar at 1573, 1673 and 1773 K.

According to Reaction 3, both SiO and CO are generated from the amorphous fibre during its crystallization to β-SiC. The final mass loss measured at 1773 K is $100\Delta W/W_0 = 26.0$, which is equal to the mass loss after completion of pyrolysis calculated from the stoichiometry of Reaction 3. The TGA curves of Nicalon heated isothermally at 1573, 1673 and 1773 K under an O_2 atmosphere are given in Fig. 2. Although the TGA curve at 1573 K shows a monotonous increase in the mass, TGA curves at 1673 and 1773 K have a maximum beyond which the mass gain changes to a mass loss. The oxidation of Nicalon is represented by Reaction 4 and results in the mass gain given in Equation 5:

$$\mathrm{SiC_{1.21}O_{0.40}(s) + 2.01O_2(g) = SiO_2(s) + 1.21CO_2(g)} \qquad (4)$$

$$\Delta W = 0.226 W_0 \qquad (5)$$

The maximum in TGA curves observed at 1673 and 1773 K is caused by the pyrolysis of Nicalon. The mass loss of $100\Delta W/W_0 \simeq 1$ obtained at 1773 K is much smaller than that from the pyrolysis in an Ar atmosphere. Thus, Nicalon hardly pyrolyses under an O_2 atmosphere. This result suggests that the oxide film suppresses the pyrolysis of the non-oxidized core.

In order to clarify the effect of oxide film on the pyrolysis of Nicalon, fibre-a and fibre-b were heated rapidly to the desired temperature and were kept for 64.8 ks in an Ar atmosphere. Fig. 3 shows isothermal TGA curves of fibre-a. At 1573 and 1673 K, a mass change is not found in the TGA curves. At 1773 K, after 10 ks pyrolysis occurs severely and the final mass loss is $100\Delta W/W_0 = 22.0$. Isothermal TGA curves of fibre-b are given in Fib. 4. The measured values fluctuate around $100\Delta W/W_0 \simeq 1$ at all temperatures. As $W_0 = 1$ g, $100\Delta W/W_0 = 1$ corresponds to a mass change of 1 mg, which is within the limits of experimental error; therefore the oxide film formed by the oxidation treatment at 1773 K suppresses nearly completely the pyrolysis of Nicalon.

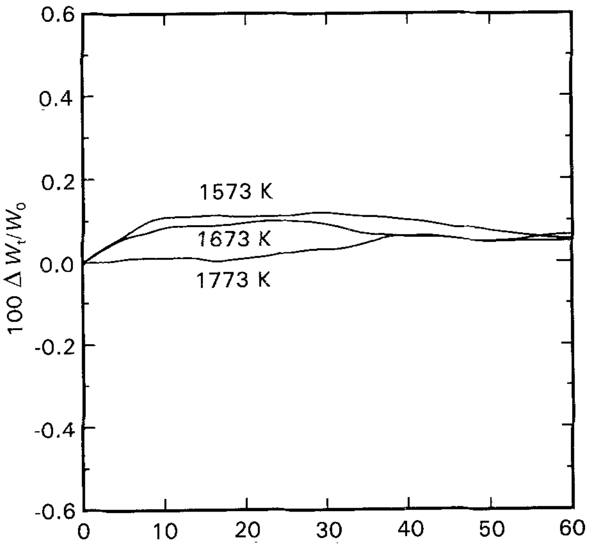

Figure 4 Mass change of fibre-b (Nicalon oxidation-treated at 1773 K) heated in Ar at 1573, 1673 and 1773 K.

3.2. X-ray diffraction patterns

Fig. 5 shows XRD patterns of original fibre and the fibres heated in an Ar atmosphere. The XRD pattern of original fibre is very broad and indicates the amorphous state, whereas XRD patterns of the heat-treated fibres are sharp and indicate crystallization to β-SiC. This XRD result substantiates the occurrence of the pyrolytic Reaction 3. XRD patterns of the fibres oxidized at 1573, 1673 and 1773 K are given in Fig. 6. At $2\theta \simeq 22°$ a broad pattern and a sharp peak coexist. The former and the latter correspond to amorphous silica and cristobalite, respectively. The peak of cristobalite becomes sharper with increasing temperature. Although the XRD patterns of β-SiC are broad, the height of its peaks increases slightly with increasing oxidation temperature. This is consistent with the TGA curves shown in Fig. 2 and shows that Nicalon pyrolyses slightly during oxidation.

Figs 7 and 8 show XRD patterns of fibre-a and fibre-b, respectively, heated in an Ar atmosphere. The patterns are broad except for fibre-a heated at 1773 K, which crystallizes completely to β-SiC. At $2\theta \simeq 22°$ the as-oxidized fibre-b has a small peak of cristobalite together with a broad pattern of amorphous silica. Although the as-oxidized fibre-a shows only the pattern of amorphous silica, the peak of cristobalite appears at $2\theta \simeq 22°$ after heating under an Ar atmosphere. This peak becomes higher with increasing temperature of heat treatment. It follows that the amorphous oxide film crystallizes to cristobalite on heating in an Ar atmosphere.

3.3. SEM observation

Fig. 9 shows SEM photographs of Nicalon heated under an Ar or under an O_2 atmosphere at 1773 K. A remarkable coarsening of β-SiC crystals is observed

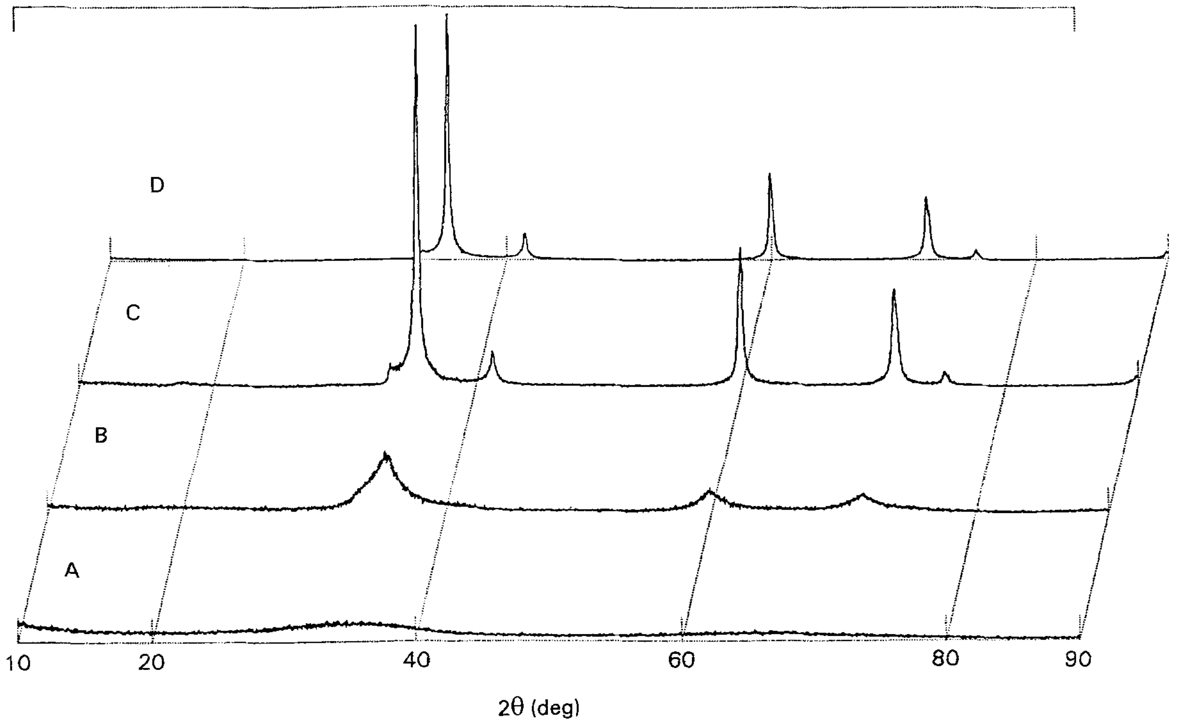

Figure 5 X-ray diffraction patterns (CuK_α) of (A) original Nicalon and Nicalon heated in Ar at (B) 1573 K, (C) 1673 K and (D) 1773 K for 64.8 ks.

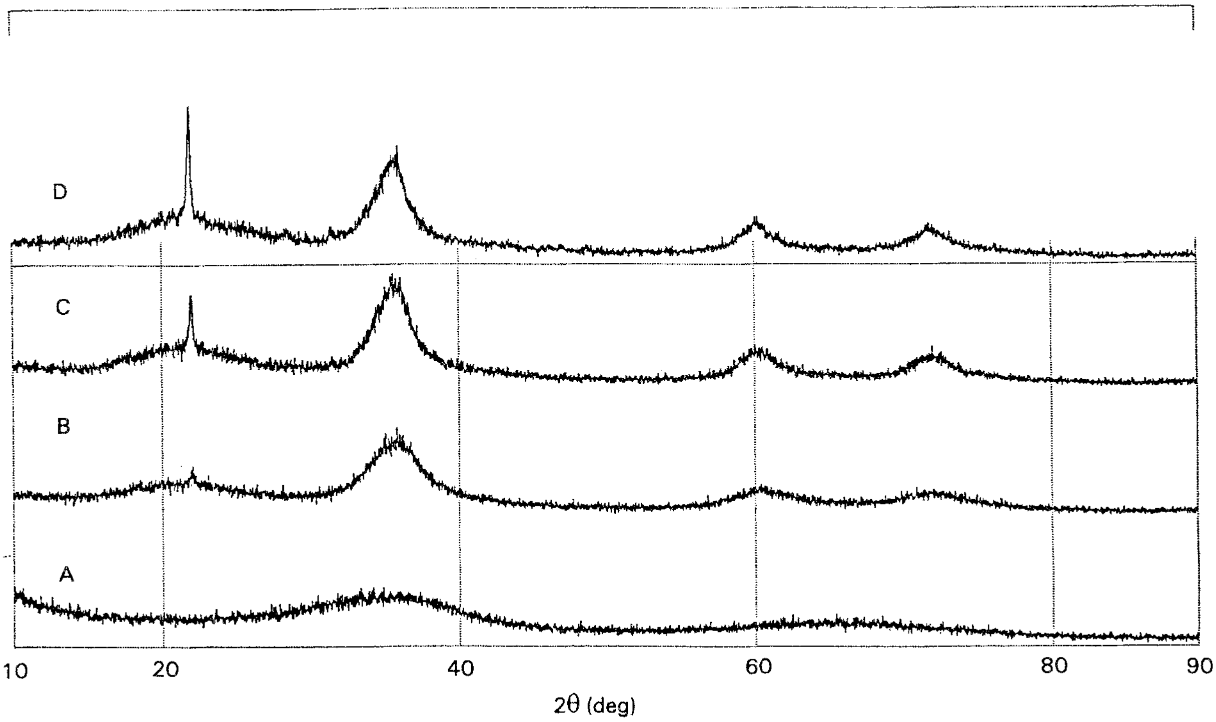

Figure 6 X-ray diffraction patterns (CuK_α) of (A) original Nicalon and Nicalon heated in O_2 at (B) 1573 K, (C) 1673 K and (D) 1773 K for 64.8 ks.

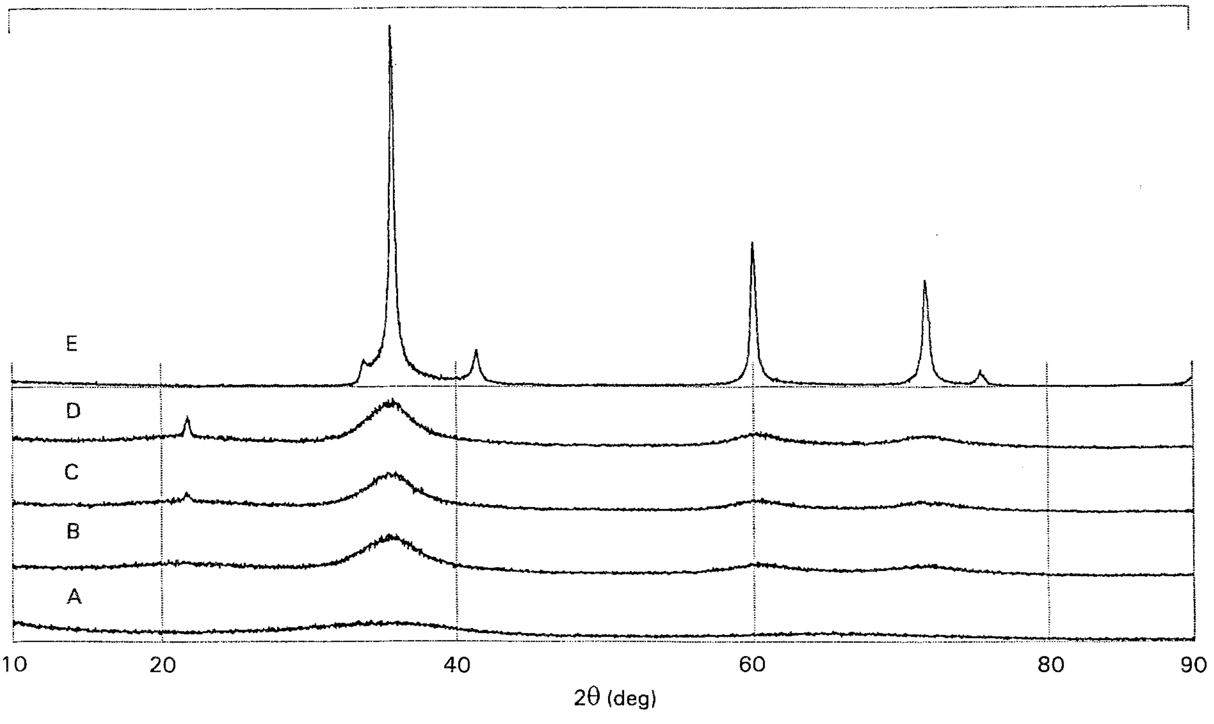

Figure 7 X-ray diffraction patterns (CuK_α) of (A) original Nicalon, (B) as-received fibre-a and fibre-a heated in Ar at (C) 1573 K, (D) 1673 K and (E) 1773 K for 64.8 ks.

both in the core and at the surface of Nicalon heated in Ar (Fig. 9a and b). The core of Nicalon oxidized is smooth and the growth of β-SiC is not found (Fig. 9c). Fig. 9d indicates that the oxide film is smooth and adheres tightly to the core. The rapid cooling after oxidation causes cracking of the oxide film. Fig. 10 shows SEM photographs of fibre-a and fibre-b heated in an Ar atmosphere at 1773 K. Fibre-a pyrolyses severely and the β-SiC crystals grow and coarsen, while the core of fibre-b is smooth and the growth of β-SiC is not observed. These SEM observations are consistent with the results of TGA and XRD.

3.4. Tensile strength

Fig. 11 shows the room-temperature tensile strength of fibres heated under an Ar atmosphere as a function of heat treatment temperature. Heat treatment in Ar

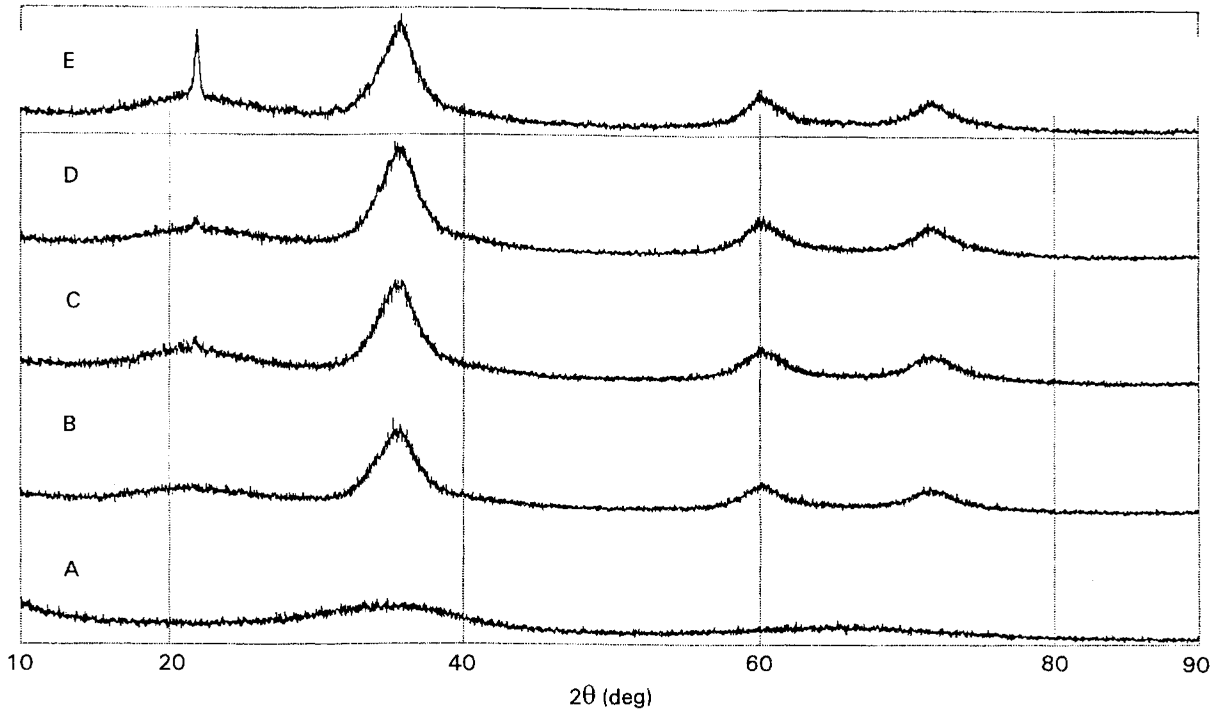

Figure 8 X-ray diffraction patterns (CuK_α) of (A) original Nicalon, (B) as-received fibre-b and fibre-b heated in Ar at (C) 1573 K, (D) 1673 K and (E) 1773 K for 64.8 ks.

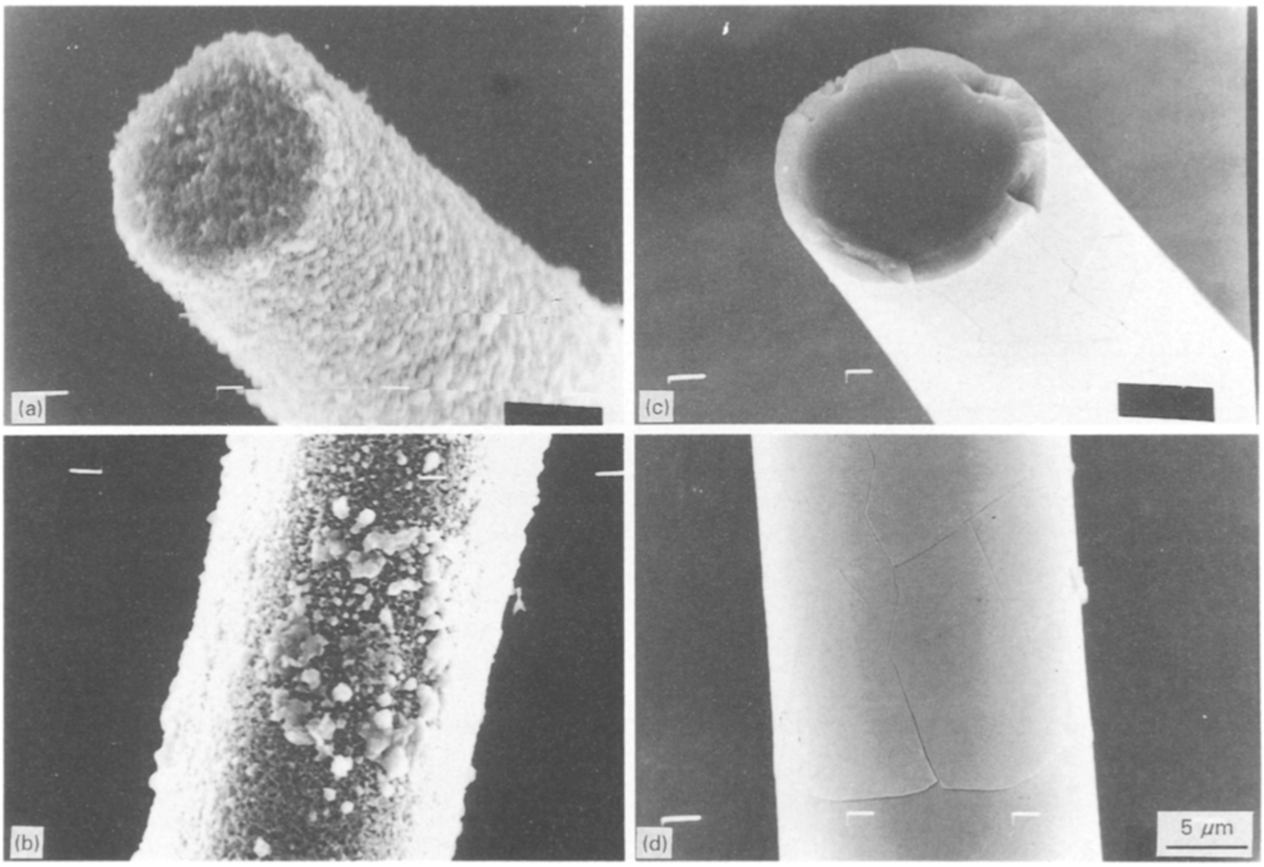

Figure 9 SEM photographs of Nicalon heated in (a, b) Ar and (c, d) O_2 at 1773 K for 64.8 ks.

causes a significant decrease in the strength of the non-oxidized fibre, and the strength of the fibre heated at 1673 K is not measurable due to complete pyrolysis. The as-oxidized fibre-a and fibre-b retain 54 and 74%, respectively, of the original strength of 2.3 GPa. Although there is only a small decrease of 4% in the tensile strength of fibre-a heated in Ar below 1673 K, the strength of the fibre heated at 1773 K is estimated

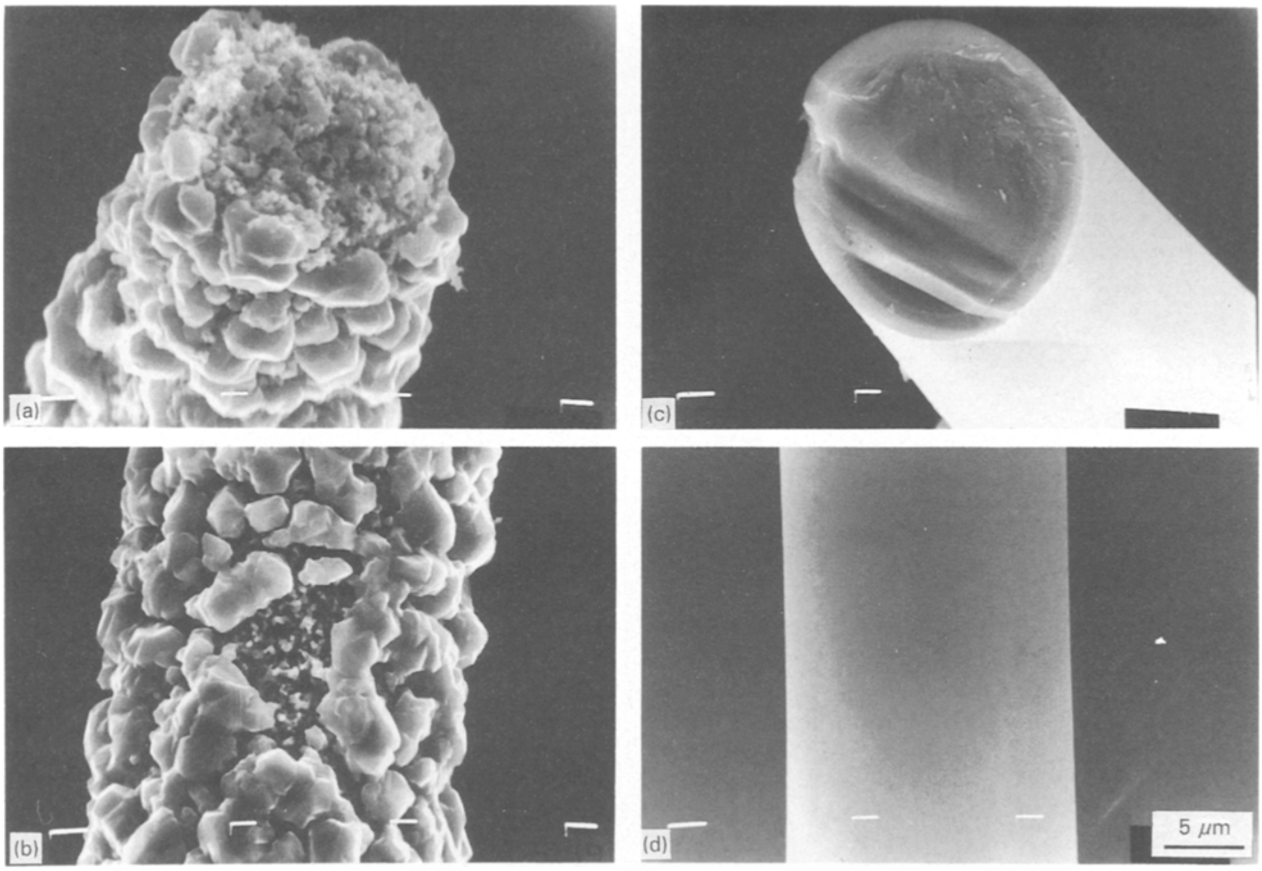

Figure 10 SEM photographs of (a, b) fibre-a and (c, d) fibre-b heated in Ar at 1773 K for 64.8 ks.

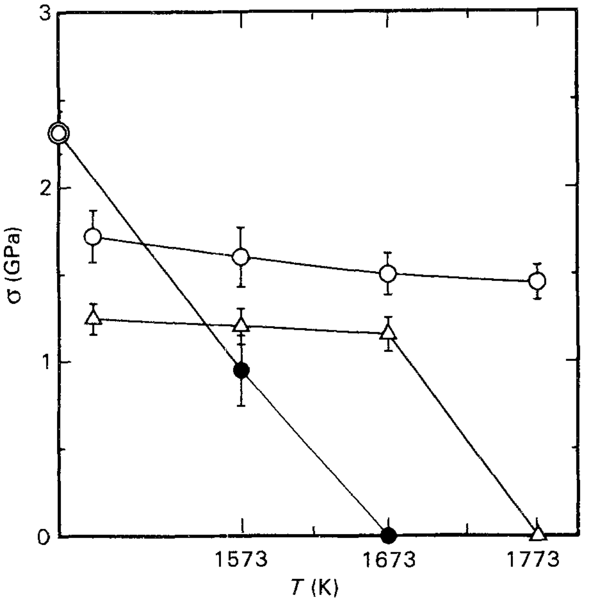

Figure 11 Tensile strength of (●) original Nicalon, (△) fibre-a and (○) fibre-b heated in Ar for 64.8 ks as function of temperature.

to be close to 0 GPa. On the other hand, fibre-b heated at 1773 K retains 63% of the original strength, i.e. 1.5 GPa.

4. Discussion

It is obvious from TGA curves, XRD patterns and SEM observation that Nicalon, which pyrolyses severely in an Ar atmosphere, decomposes hardly at all during oxidation. At elevated temperatures, Nicalon must decompose essentially according to the pyrolytic Reaction 3, independent of the kind of atmosphere. It is therefore considered that under an O_2 atmosphere the oxide film formed around Nicalon prevents the generation of SiO and CO from the core. This is substantiated by the fact that the pyrolysis of Nicalon previously oxidized at 1573 and 1773 K, i.e. the decomposition of fibre-a and fibre-b, is suppressed nearly completely.

The diffraction patterns of β-SiC in the as-oxidized fibre (fibre-a and fibre-b) become a little sharper than that of the amorphous original fibre. The tensile strength of the as-oxidized fibre is lower than that of the original fibre. This is because Nicalon pyrolyses as a result of imperfect coating with oxide film at the early stage of oxidation. The kinetics of oxidation changed from the rate equation for reaction control to that for diffusion control [16]. When a continuous layer of silica is formed around Nicalon, the oxidation rate is determined by the solid-state diffusion of oxygen through the silica layer and pyrolysis of the core is suppressed.

Fig. 12 shows SEM photographs of fibre-a and fibre-b in the as-oxidized condition. There are many cavities at the surface of fibre-a. The cross-sectional observation of fibre-a indicates the propagation of a crack from a cavity, i.e. a mirror-hackle fracture surface. On the other hand, fibre-b has a smooth surface and is fractured uniformly. Nicalon has a microstructure of intermixed β-SiC crystals SiO_2 and free carbon [17, 18]. Oxidation of the free carbon is initiated at a lower temperature than that of SiC. Consequently, the cavities on the oxide film of fibre-a

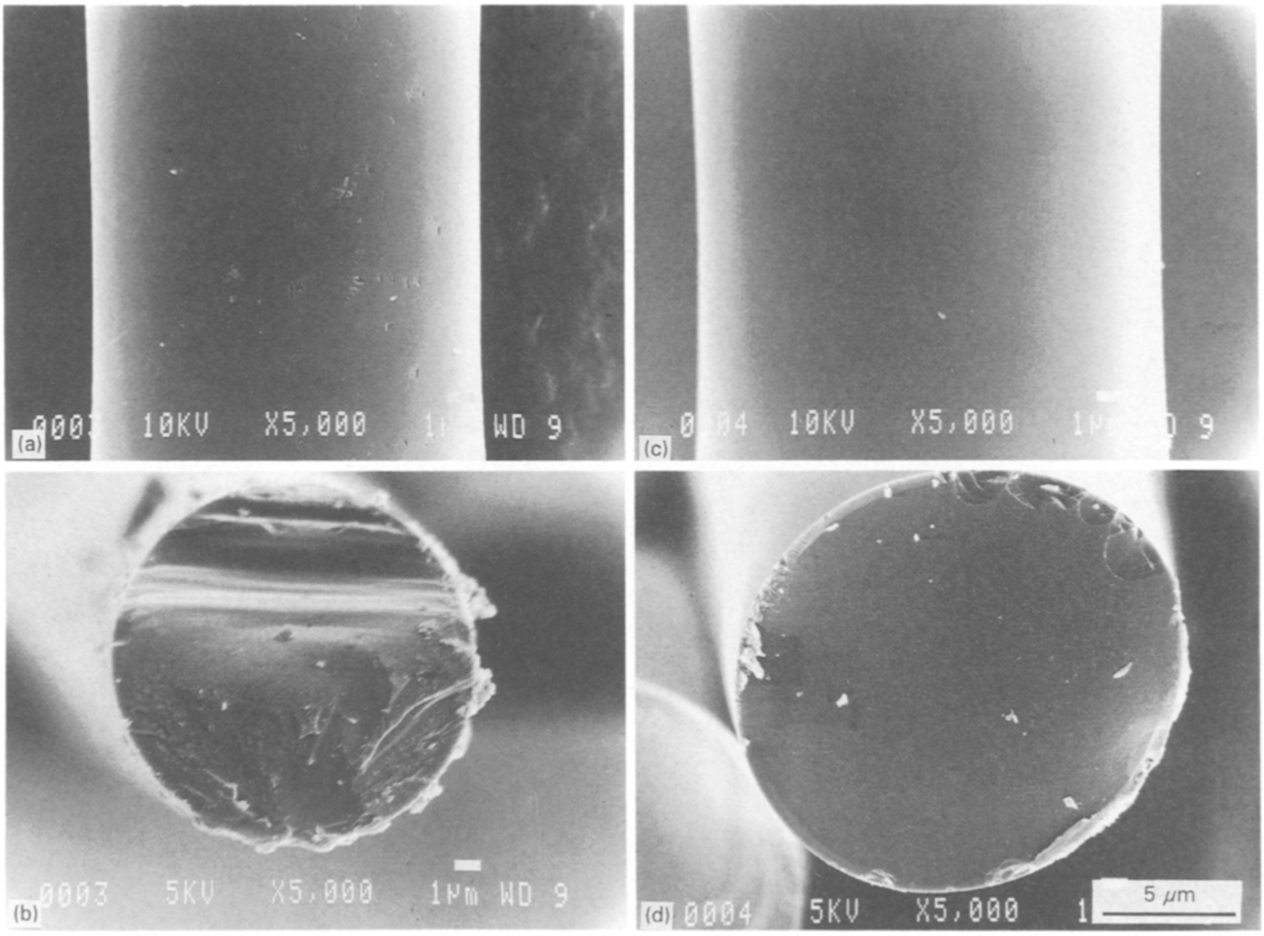

Figure 12 SEM photographs of as-received (a, b) fibre-a and (c, d) fibre-b.

oxidation-treated at the lower temperature of 1573 K are due to the preferential oxidation of free carbon. The cavities are the source of some surface flaws on the non-oxidized core beneath the oxide film. Since the oxidation kinetics for SiC becomes sufficiently rapid to oxidize concurrently both SiC and free carbon at 1773 K, the oxide film of fibre-b is smooth and hence surface flaws may be absent from the core of the fibre. Correspondingly, the tensile strength of fibre-a is lower than that of fibre-b, as shown in Fig. 11.

After heating at 1773 K under an Ar atmosphere, fibre-a pyrolyses completely to crystallize into β-SiC, although the pyrolysis of fibre-b is suppressed. This result is due to the difference in the condition of the oxide surface layer on Nicalon, as mentioned above. Fibre-b does not pyrolyse at 1773 K, because the evolution of SiO and CO from the core is prevented by the oxide film which is free from surface flaws. Fibre-a pyrolyses severely because high-pressure gases of SiO and CO break the weak oxide film and escape through the cracks. Below 1673 K the pyrolysis is suppressed because of the lower pressure of SiO and CO evolved. As shown in Figs 7 and 8, the film of amorphous silica crystallizes quickly to cristobalite in an Ar atmosphere with increasing heating temperature. The crystallization also causes surface defects on the oxide film which then result in pyrolysis of the fibre. Consequently, the tensile strength decreases slightly on heating fibre-a up to 1673 K and fibre-b up to 1773 K, as shown in Fig. 11.

When Nicalon coated with the oxide film is heated at the higher temperature, the non-oxidized core has a tendency to pyrolyse. Cracks are produced in the oxide film because the strength of the oxide film cannot withstand the decomposition pressure from the core. During the escape of CO gas through the cracks, Reaction 6 occurs between CO and SiO_2:

$$SiO_2(s) + CO(g) = SiO(g) + CO_2(g) \qquad (6)$$

This reaction is supported by the fact that the peaks of SiO_2 are not found in XRD patterns of fibre-a heated at 1773 K. Finally, the overall reaction for reduction of the oxide film is represented by the following reaction:

$$SiC_{1.21}O_{0.40}(s) + 1.81SiO_2(s) = 2.81SiO(g) + 1.21CO(g) \qquad (7)$$

The pyrolytic reaction becomes highly active as a result of the disappearance of the oxide film. Consequently a rapid mass loss is observed after heating fibre-a at 1773 K for about 10 ks, as shown in Fig. 3.

5. Conclusions

The thermochemical stability of Nicalon NL400 was investigated and the following results were obtained:

1. Under an Ar atmosphere, Nicalon pyrolysed severely. Remarkable coarsening of β-SiC crystals was observed.

2. Under an O_2 atmosphere the pyrolysis of Nicalon was suppressed by the formation of an oxide film. The amorphous oxide film crystallized to cristobalite on prolonged heating at high temperatures. Consequently the pyrolytic reaction occurred only slightly and the core became microcrystalline.

3. Nicalon coated with the oxide film was stable and had appreciable tensile strength after rapid heating to a high temperature under an Ar atmosphere. In particular, Nicalon which was oxidation-treated at 1773 K retained 63% of the original strength after heating at 1773 K. The decrease of the strength was due both to the formation of flaws on the oxide film during oxidation treatment and to crystallization of the oxide film to cristobalite during heating under an Ar atmosphere.

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