JOURNAL OF MATERIALS SCIENCE **36** (2001) 2931–2935

Improvements in refractoriness and properties of Nicalon fibres by high-temperature heat-treatment

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Nicalon SiC fibres were heat-treated in various atmospheres and at various pressures. Initially CO, nitrogen and air were used as the heat-treatment environment at one atmosphere pressure. Microstructural changes and any related strength degradation or improvement were measured for the heat-treated fibres. After heat-treatment in the temperature range 1000°C–1600°C, each sample showed different weight changes. Thus, in air, a weight gain was observed with increasing temperature, whereas in CO and N_2, weight losses were observed but with a smaller weight loss observed for CO. Moreover, carbon monoxide had a significant effect on the strength retention of the fibres. Since the lowest weight loss was observed after heat-treatment in CO at one atmosphere, high pressure CO gas was used to heat-treat Nicalon fibres between 1000°C and 1700°C and the resulting fibres were analysed by single-filament strength testing, scanning electron microscopy, and X-ray diffraction. The results were completely different compared with those in one atmosphere of CO. As the temperature increased, weight and strength increased whereas at one atmosphere pressure, both weight and strength had decreased. The weight increase was because of surface reaction between the CO atmosphere and the SiC fibre and/or because of deposition of carbon from the pressurised CO gas, giving the fibre a surface carbon coating. Carbon coating of a fibre is a beneficial property for CMCs since it provides a weak interface which facilitates pull-out during fracture.

1. Introduction

A common problem found with fibres based on PCS or other pre-ceramic polymers is the residual oxygen left in the fibre after processing. Normally this excess oxygen resides in the boundaries between SiC grains. Dow Corning found that ceramic fibres formed via a polymer route and containing excess oxygen, tended to have a porosity problem. The excess oxygen results in subsequent processing problems and as shown later causes instability in the fibre under certain conditions. The majority of oxygen found in the final fibre comes from oxygen introduced either during the synthesis of the pre-ceramic polymer, or interjected into the polymer in order to cross-link the fibre and make it infusible

Residual porosity can be related to the polymer yield during conversion. During the high temperature conversion of these polymers to a ceramic, a considerable amount of weight loss occurs due to the loss of organic gases. This outgassing causes surface pits and internal porosity in the fibre. Work done at Dow Corning [1, 2] and by Sawyer [3, 4] correlated these defects, porosity and surface pits, as well as the effects of inclusions and surface damage with the limitation in fibre strength. These findings indicate that the strength limiting mechanisms in Nicalon fibres result from flaw-controlled brittle fracture. It is concluded that the smaller the flaws the higher the fibre strength, and that the flaws at or near the surface are the most severe.

Mah *et al.* [5] investigated the degradation of Nicalon SiC fibres in different atmospheres and temperatures. At high temperatures, changes in the fibre chemistry occurred resulting in weight loss (CO evolution) and SiC grain growth. Fibres heat-treated in air and argon at 1200°C underwent a degradation in tensile strength. They concluded that the strength reduction observed in the heat-treated fibres was due to evolution of carbon monoxide (CO) gas from the surface of the fibre. As explained above, these Nicalon fibres contain excess carbon after processing. The oxidation of this excess carbon from the fibre leaves surface pits, resulting in drastic loss of strength. Chaim and Heuer [6] have reported that α-SiC crystallites precipitate in the Nicalon fibre microstructure at 1200°C under an argon atmosphere after 12 hours and they observed the presence of pores which were attributed to oxidation of excess carbon in the fibre.

Jaskowiak and DiCarlo [7] examined the effect of pressure on the thermal stability of Nicalon fibres. They heat treated Nicalon fibres under three different pressures, vacuum (10^{-9} MPa), ambient pressure (0.1 MPa) and an over pressure (138 MPa), at temperatures ranging from 1000 to 1500°C. In the over pressure conditions, they found that the fibres were able to withstand 1500°C for one hour without strength or weight change. It is believed that this observed retention of strength was due to the stabilisation of the Si-C-O containing regions of the fibre. At high temperatures the over pressure inhibited the evolution of CO and SiO gas from the fibre surface, thereby stabilising the fibre microstructure.

Coustumer [8] has reported that the polycarbosilane based NL-200 fibres consist of three microstructural constituents: ß-SiC grains, turbostratic carbon stacks, and amorphous silicon oxycarbide $SiO_{1.15}C_{0.85}$. Both SiC and C phases are nanometric and dispersed, while the silicon oxycarbide is a chemical and physical continuum which acts as an intergranular phase. The thermal degradation mechanism follows a two step procedure which can be summarised as an endogenous (i.e. self-induced) oxidation mechanism, providing gaseous SiO and CO. Simultaneously, SiC grains increase in size, first slowly, then more rapidly, also following a two step mechanism [8, 9]. Heat treatment experiments in a variety of atmospheric conditions were performed on NL-200 fibres at atmospheric pressure by Coustumer *et al.* [10] the temperature range being chosen to be that in which fibre degradation occurs. They observed that in an alumina furnace tube environment, the fibres underwent the endogenous oxidation mechanism as described by reactions (1.1, 1.2 and 1.3), i.e. :

$$SiO_{1.15}C_{0.85} \Rightarrow SiO + 0.15CO + 0.7C \quad (1.1)$$

$$SiO + 2C \Rightarrow SiC + CO \quad (1.2)$$

or

$$0.75SiO_{1.15}C_{0.85} + 0.42C$$

$$\Rightarrow 0.24SiO + 0.56CO + 046SiC \quad (1.3)$$

In carbon furnace conditions (10 Pa partial pressure of CO), the reverse of reaction (1.2) is normally observed i.e.:

$$SiC + CO \Rightarrow SiO + 2C \quad (1.4)$$

Another possible reaction in a higher pressure CO atmosphere at high temperatures is:

$$2CO \Rightarrow CO_2 + C \quad (1.5)$$

Heat treatment in a CO atmosphere offers an attractive route for obtaining carbon coatings on the fibres if reactions (1.4) or (1.5) take place. This is often necessary for specific purposes to assist fibre/matrix compatibility or achieve improved toughness.

2. Experimental procedure

The fibres used in this investigation were Nicalon NLM 207 ceramic grade fibre from Nippon Carbon, Japan. The polyvinyl acetate sizing was removed by a 2 h heat treatment at 500°C in air. It has been established that this method of desizing does not influence the initial strength distribution of as-received fibres. Heat treatment of the Nicalon SiC fibres was carried out at either atmospheric pressure or high pressure. Initially, fibres were heat-treated in the temperature range 1000–1600°C under atmospheric nitrogen, carbon monoxide or air for 30 min. For high pressure heat-treatment, 45 bar CO gas was used to suppress CO volatilisation.

After heat treatment, the tensile strength of single heat-treated fibres and as-received fibres was measured using a load hanging system. 10 fibres were measured to minimise error. A scanning electron microscope (S2400, Hitachi, Japan) was used to examine heat-treated fibre surfaces. X-ray diffraction was carried out on as-received and heat-treated fibres but no diffraction pattern was observed.

3. Results and discussion

3.1. Heat treatment at atmospheric pressure

Nicalon fibres were heat treated in one atmosphere of N_2, CO and air in the temperature range 1000–1600°C. Table I and Fig. 1 show the weight loss (or gain) after heat treatment. Whilst heat treatment in both N_2

TABLE I Heat treatment of Nicalon fibres for 30 minutes at 1 atmosphere pressure

Temp. (C°)	Weight loss in N_2 (%)	Weight loss in CO (%)	Weight gain in Air (%)
1000	0	0	0.4
1100	0.2	0.05	0.4
1200	0.2	0.05	0.70
1300	0.3	0.2	0.8
1400	0.5	0.4	1.4
1500	1.01	0.8	2.0
1600	7.6	2.5	3.4

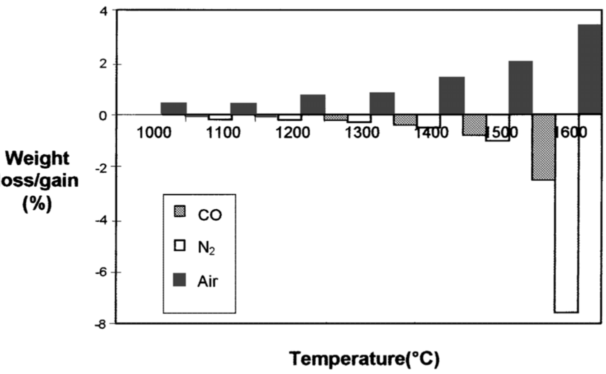


Figure 1 Weight loss of Nicalon fibres after heat treatment at 1 atmosphere pressure.

and CO resulted in weight loss, heat treatment in air led to a weight gain because of fibre oxidation. The reason why weight loss occurred in a non-oxidising atmosphere is because of decomposition of the silicon oxycarbide grain-boundary material into CO and SiO as described by reactions (1.1) and (1.2). However, the amounts of these two gases differ in different environments since a CO gas atmosphere suppresses volatilisation of CO from the fibres. Whilst this effect is small at lower temperatures, at higher temperatures the differences are much larger. Thus at 1600°C, the weight loss during CO heat treatment is 2.5% whereas the weight loss in N_2 is 7.6%. It is obvious that CO gas is a better environment than N_2 in terms of fibre degradation. Since the minimum weight losses occurred with CO heat treatment, high pressure heat treatment in CO gas was chosen for further studies.

3.2. Heat treatment of SiC fibres in high pressure CO

Nicalon SiC fibres were heat-treated in high pressure CO in the temperature range 1000–1600°C for 30 min so as to suppress CO volatilisation from the fibres and to improve fibre properties. For this purpose, a gas pressure sintering furnace operating at a safety limit of 50 bar was used. The results are tabulated in Table II. Although heat-treatment at one atmosphere pressure of CO caused a weight loss, heat-treatment at 45 bar led to a weight gain. Moreover, the weight gain started at 1400°C for high pressure heat-treatment whereas the weight loss started at 1100°C for atmospheric pressure treatment. The usual fibre degradation was prevented but another reaction took place which resulted in a weight gain. As shown in Fig. 2c and d, this reaction caused a shell to form on the fibre surface above 1500°C. The very small thickness ($\approx 1\ \mu$m) of this layer made it difficult to characterise. Of the three possibilities: SiC, SiO_2 and C, SiC would have given negligible SEM contrast; silica would be unlikely to form under the high Pco conditions used (and would have reacted with grain boundary glass during subsequent composite fabrication—a situation which was not observed). It is therefore most likely that the shell consisted of deposited carbon. Carbon formation can be explained by reaction 1.4 but in this case a weight loss would have been observed due to the volatilisation of silicon monoxide. A more likely explanation would involve deposition of carbon from the pressurised carbon monoxide gas, as given by reaction 1.5. This carbon layer would act as an inert coating to prevent chemical reaction between fibres and matrix as observed in subsequent experiments. Not only is this expected from the experimental conditions, but it would also give rise to a weight gain as observed. Even though the weight gain began above 1300°C (Table II), visible shell formation started at 1500°C (Fig. 2).

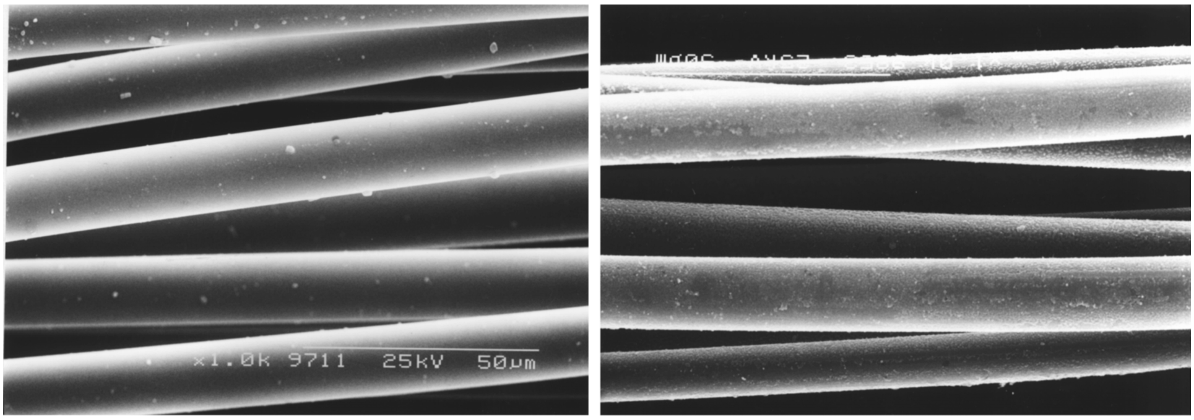
TABLE II Property changes after heat treatment of SiC fibres at 45 bar CO pressure for 30 minutes at various temperatures

Temp. (C°)	Pressure (bar)	Weight gain (%)	Heat-treated fibre strength (GPa)
As rec.	—	—	2.80
1000	41	0	3.77
1100	43	0	4.17
1200	44	0	4.13
1300	45	0	3.13
1400	45	0.6	3.77
1500	46	1.5	4.05
1600	46	6.5	3.91
1700	47	18.5	—

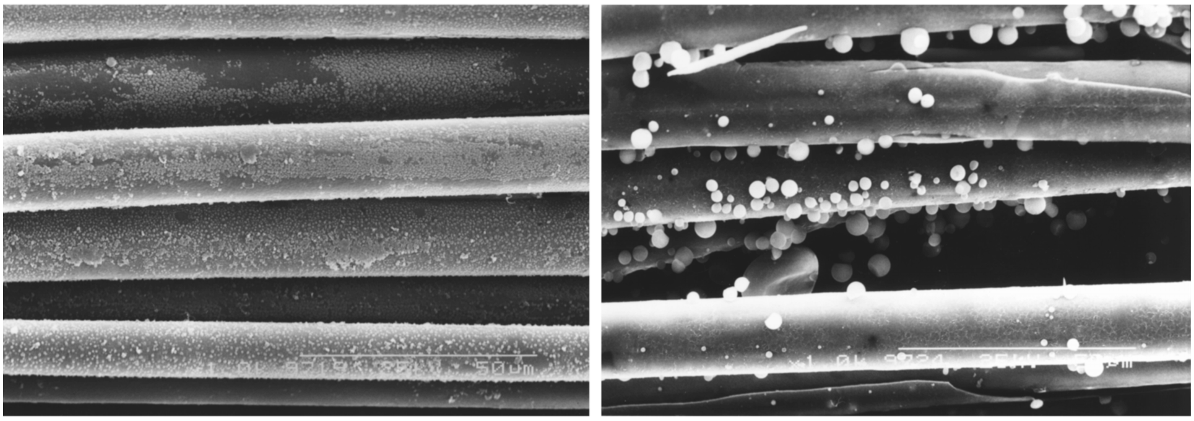
Many researchers have observed that up to 75% of the fibre strength can be retained on heat-treatment at temperatures up to 1300°C in a CO-containing atmosphere, but no one has observed a strength increase for Nicalon fibres heat-treated in pure CO. On high pressure heat treatment, it was expected that the original fibre strength might be retained, but it was very surprising to observe that in general a strength increase occurred. In fact at each temperature up to 1600°C, an increase in strength was observed. As shown in Fig. 3 the as-received fibre strength was 2.8 GPa. The strength of the fibres after heat-treatment at 1000°C was 3.7 GPa, 32% higher than the as-received value. At 1100°C the heat-treated fibres reached a maximum strength of 4.2 GPa which represents a 50% overall strength increase. At this point the strength started to decrease as weight gains were observed associated with shell formation. However, between 1300 and 1400°C the strength of the fibres began to increase again, with weight gain and shell formation occurring, reaching another peak at 1500°C, representing an increase of 42% compared with the as-received fibres; weight gain and shell formation also started to increase sharply at this temperature. Above 1600°C, fibre strength decreased sharply because of the increasing fibre shell thickness and corresponding decrease in fibre diameter due to weight loss. The microstructure of the fibre became porous under the shell at 1700°C. The use of high pressures of CO suppressed degradation up to 1600°C but after this point, the fibre degraded suddenly and measurement of fibre strength at 1700°C became impossible.

As well as shell formation, glass-like materials were deposited on the shell. As shown in Fig. 2d this material occurred in the form of small drops which later coalesced into larger drops. The wettability of this material with respect to the fibre shell seems very poor. This is also a beneficial property for CMCs because a non-adherent interface inhabits chemical reactions. However, the most important property for CMCs is the shell formed around the fibre because this can perform the role of a coating. Coated fibres are preferred because they decrease the interfacial shear strength, and whilst it is possible to coat monofilament fibres, it is very difficult to coat fibre tows uniformly. Thus, as well as increasing the strength, a uniform carbon coating is obtained by the high pressure CO heat treatment at high temperatures. This is especially helpful for fibre pullout during fracture of CMCs since it provides a mechanism for crack deflection.

Nicalon fibres were also heat-treated in 45 bar of N_2 pressure at 1600°C for 30 min in order to compare



(a) as-received (b) 1500°C



(b) 1600°C (d) 1700°C

Figure 2 Nicalon fibres heat-treated at 45 bar pressure for 30 minutes at various temperatures.

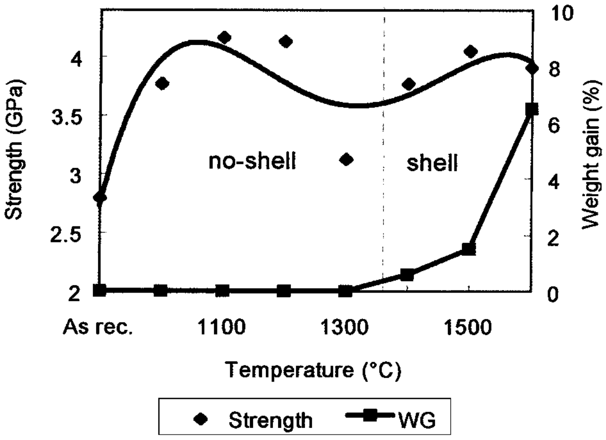


Figure 3 Fibre strength variation after high pressure CO heat treatment.

with the high pressure CO heat-treatment Only 1.1% weight loss was observed whereas at one atmosphere of nitrogen pressure the heat treated fibres had shown a weight loss of 7.6%. Clearly, the high pressure N_2 heat-treatment is also beneficial for the fibres. Whilst a surface reaction was observed for CO heat treatment, after N_2 heat treatment no such surface reaction was observed. However, when compared with CO, the strength of the N_2 heat-treated fibres was much lower than the equivalent CO values in spite of the surface reaction. This is most probably because of some decomposition of the silicon oxycarbide phase accompanied by grain growth of the ß-SiC grains in the high pressure N_2.

4. Conclusions

CO is the most beneficial gaseous environment for Nicalon fibre heat treatment in terms of preventing fibre degradation since it suppresses CO volatilisation. High pressure CO heat treatment has revealed important findings as a result of which fibre strength can be increased in the temperature range 1000–1500°C. As well as the strength increasing, at higher temperatures a shell forms on the fibre surface which acts as a coating. Whereas this surface reaction is observed after CO heat treatment, N_2 heat treatment results in no surface reaction. When compared with the CO results, the strength of the N_2 heat-treated fibres is much lower than after CO treatment in spite of the surface reaction taking place.

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Received 10 May
and accepted 29 December 2000