JOURNAL OF MATERIALS SCIENCE 26 (1991) 5075–5080

Effect of carbon monoxide partial pressure on the high-temperature decomposition of Nicalon fibre

G. S. BIBBO*, P. M. BENSON, C. G. PANTANO
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

The high-temperature equilibrium partial pressures of the predominant gaseous species over Nicalon were determined thermochemically. It was calculated that the most prevalent gaseous species in equilibrium with Nicalon at 1300 °C is carbon monoxide. Subsequently, fibres of Nicalon (NLM 202) were heat treated at 1300 °C in various partial pressures of carbon monoxide gas and analysed via single filament strength testing, scanning electron microscopy, X-ray diffraction, and scanning Auger microscopy. The heat treatments in carbon monoxide had a significant effect on the strength retention and composition of the fibres (~75% retained) compared to the treatments in argon where only 25% of the initial strength was retained. The Auger analysis revealed that the treatment in argon evolved carbon and oxygen from the fibre while in carbon monoxide atmospheres a carbon layer was deposited on the fibre surface. X-ray diffraction showed that grain growth had not occurred in any of the heat treatments. This study shows the important role of thermochemical reactions in the strength degradation of Nicalon, and its possible relationship to the formation of carbon surface/interface layers.

1. Introduction

Nicalon fibre has been the subject of much research in recent years stemming from its potential as a high-temperature reinforcement material [1–18]. These fibres can impart high toughness to certain glass-ceramic composites due to the formation of a carbon interphase [1]. This interfacial carbon phase dramatically increases the work of fracture by promoting crack deflection, frictional debonding and fibre pull-out [19]. The mechanism of the carbon formation is not well understood. Because this carbon layer is less prevalent or non-existent in composites reinforced with other silicon carbide materials, its formation is believed to be related specifically to the composition and structure of Nicalon fibres [2]. It is for this reason that a better comprehension of the structure, composition, and thermal stability of Nicalon and related fibres is needed.

Pioneering studies by Yajima and co-workers reported the Nicalon fibre structure as a fine-grained microcrystalline silicon carbide with excess carbon and oxygen [3]. Recently, more detailed analyses using various analytical techniques have expanded this description [4–7]. These studies suggest a fibre structure containing 1–3 nm silicon carbide microcrystals with clusters of polymaromatic carbon, and silica with evidence of an oxycarbide phase. A structural model based on a continuum of SiC_4 and SiC_xO_y $(x + y = 4)$ with a surface SiO_2 layer and arbitrary regions of carbon aggregates has been proposed.

The formation of this unique microstructure is a direct result of the polycarbosilane precursor and processing techniques used to manufacture the fibre [5], i.e. it is thermodynamically metastable. As a result, fibres decompose after only short thermal exposures above 1200 °C, exhibit grain growth at higher temperatures and, most importantly, they experience a decrease in strength. Many researchers have investigated the effect of high-temperature heat treatment on fibre strength retention in various environments [8–12]. It was found that fibres heat treated in inert environments (Ar, N_2, vacuum) showed severe degradation caused by the extensive outgassing of decomposition products. Fibres treated in an oxidizing environment (O_2, air) showed slightly less degradation.

Thermodynamic descriptions of the high-temperature instability of Nicalon have been attempted by several researchers. For instance, calculations by Luthra [13] indicate that Nicalon is of non-equilibrium composition resulting in an intrinsic degradation at high temperatures with the predominant decomposition product being carbon monoxide gas. High-temperature outgassing studies by Mah *et al.* [10] also reported that CO(g) is the main decomposition product at high temperatures. In contradiction, two Knudsen cell mass spectroscopy (KCMS) studies by Johnson *et al.* [14, 15] have reported that SiO(g) is the

---

* Now with GTE Products, Manchester, NH, USA

0022–2461/91 $03.00 + .12

predominant vaporization species. These discrepancies have never been explained, but may be due in part to variations in the composition and thermal history of the fibres examined.

Altogether, the current literature on Nicalon, and Nicalon-reinforced composites, points to the need for a correlated study of the thermochemistry, surface chemistry, and strength behaviour of heat-treated Nicalon. Consequently, the purpose of this investigation was to examine the relative effects of heat treatment on the surface chemistry and strength degradation of Nicalon. The heat-treatment atmospheres were defined by calculations of the equilibrium partial pressure of gas phase decomposition products.

2. Experimental procedure

2.1. Thermochemical calculations

The thermodynamic calculations were performed using the computer program SOLGASMIX written by Eriksson [20]. The program uses thermodynamic data of individual species (ΔH_f^0 and ΔS_f^0) including fixed composition condensed species, condensed solutions, and gaseous solution species [21, 22]. The algorithm iterates molar amounts until the total free energy of the system is minimized. Thermochemical models which are assumed for the gas and glass solution phases (containing mixtures of liquid stoichiometric compounds) are described elsewhere [23]. The activities of the condensed species are assumed to be unity in this analysis.

2.2. Materials

The fibres used in this investigation were Nicalon NLM 202 ceramic grade fibres from lot 032. The polyvinyl acetate sizing was removed via a 2 h heat treatment at 500 °C in oxygen. It was verified that this method of desizing does not influence the initial strength distribution of the as-received fibres.

2.3. Heat treatments

Lengths of desized fibre tows of 10 cm were supported in a high-purity alumina boat so that only the ends were in contact with the boat surfaces. The boat was placed in a SiC tube furnace heated via $MoSi_2$ elements. The furnace atmosphere was contained by stainless steel and glass tubing and connected with VCR fittings. Precise mixtures of UHP gettered argon ($< 10^{-9}$ p.p.m. O_2) and ultra-high purity carbon monoxide were achieved using MKS Instruments Model 297B mass flow controllers. Samples were heated at 20 °C $\min^{-1}$ to 1300 °C and held for 30 min in 1 atm total gas pressure ($P_{CO} + P_{Ar} = 1$ atm) at a total flow rate of 500 standard $cm^3 \min^{-1}$. Carbon monoxide partial pressures investigated were 0.0, 0.07, 0.2, 0.3, 0.4, 0.5, 0.8, and 1.0 atm.

2.4. Strength testing

Single filaments were separated from as-treated tows and only straight fibres with no obvious change in filament diameter along the length were selected for strength measurements. Individual filaments were aligned with the centreline of a 1 cm × 2 cm cardstock tab and mounted to one end with Conap epoxy in a method outlined previously [12]. A segment of each test filament was removed for diameter measurement in the SEM (ISI-SX40A) at ×2500. Fibres were loaded on an Instron tensile tester using a 50 g load cell, 1 in. (2.54 cm) gauge length, and a crosshead speed of 0.05 mm $\min^{-1}$. A minimum of 30 fibres was tested per condition to provide statistical significance to the results.

2.5. Fibre analysis

Segments of test specimens were mounted on aluminium holders and sputter coated with gold for scanning electron microscopy (SEM) analyses. For X-ray diffraction (XRD) analysis, fibre specimens were ground to -200 mesh in an agate mortar. XRD was performed using CuK_α radiation at a scan speed of 10° $2\theta \min^{-1}$ on a Rigaku Geigerflex. Scanning Auger microscopy (SAM) was performed on a Jeol JAMP30 scanning Auger microprobe. The electron beam diameter was nominally 0.5–0.7 μm in these analyses. The depth profiles were acquired using a 2 keV argon ion beam at a sputter rate of 16 nm $\min^{-1}$ as determined by calibration using a 100 nm thick silica film on a silicon wafer. The relative sensitivity factors for quantitative analysis of silicon, carbon and oxygen were determined using the spectra obtained after sputtering into the bulk of the fibre (assuming a Nicalon composition of 39 at % Si, 49 at % C, and 12 at % O) [16]. The absolute values of these quantitative analyses may be in error due to sputtering effects, but nevertheless the relative changes observed in the fibre surface composition profile are genuine representations of the heat-treatment effects.

3. Results

3.1. Thermochemical analyses

The calculations assumed a fibre composition of 39% Si, 49% C and 12% O. Fig. 1 shows that this composition at equilibrium lies in the three phase region of

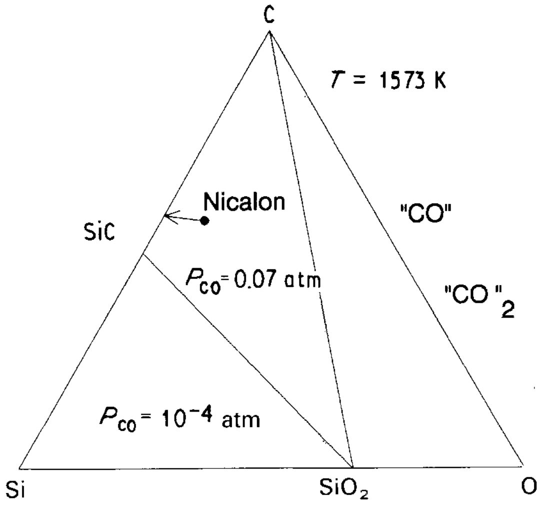

Figure 1 Diagram of the ternary system Si–C–O at 1300 °C.

SiO_2–SiC–C. According to the phase rule, this region has zero degrees of freedom. Therefore, the partial pressures of the gas phases are constant over the entire region (for any given temperature); i.e. they are independent of fibre composition provided that the composition does not move outside the three-phase field.

The calculations revealed that the most prevalent gas in the three-phase field is CO. The equilibrium pressure at 1300 °C is ~ 0.07 atm, and it increases about an order of magnitude for each 100 °C increment in temperature. The only other gases at this temperature are CO_2 and SiO, but their pressures are several orders of magnitude less than that of CO (i.e. 10^{-4} and 10^{-7} respectively). Interestingly though, the SiO(g) pressure is predominant only for fibre compositions that lie in three-phase region Si–SiO_2–SiC. This suggests that the reports of significant SiO(g) evolution during the heat treatment of Nicalon were based on non-equilibrium conditions or on exceedingly silicon-rich compositions. These calculations indicate that if the fibre is heated in an overpressure of CO(g) equal to or greater than 0.07 atm, the decomposition reactions that create CO(g) will be reduced. Nevertheless, reactions may occur to create the equilibrium assemblage of SiC, SiO_2, and carbon phases. These reactions could change the microstructure, and thereby the strength of the fibres, but they should not change the overall composition of the fibre to any great extent. On the other hand, if the fibres are heated in a vacuum or in a flow of an inert carrier gas, the fibres will react to create the equilibrium vapour pressure of CO(g). This will necessarily lead to decomposition of the fibre and substantial changes in the composition of the fibre. In principle, the unlimited generation and escape of CO(g) would cause the fibre composition to follow the line shown in Fig. 1.

3.2. Strength analyses

The room-temperature tensile strength data for the heat-treated samples are tabulated in Table I, and are plotted as a function of the carbon monoxide partial pressure at 1300 °C in Fig. 2. The data points represent an average of 30 or more fibres per test condition with error bars represented as 95% confidence intervals. The lowest strengths were observed for fibres heated in the pure argon atmosphere (0.0 atm CO). These fibres retained only 27% of their as-received strength. In contrast, all fibres heated in CO/Ar mixtures greater than 0.07 atm CO retained 65%–80% of their as-received strength. However, differences in the strength retention between various CO/Ar mixtures were less dramatic; but, there appears to be a strength maximum at 0.4 atm CO(g).

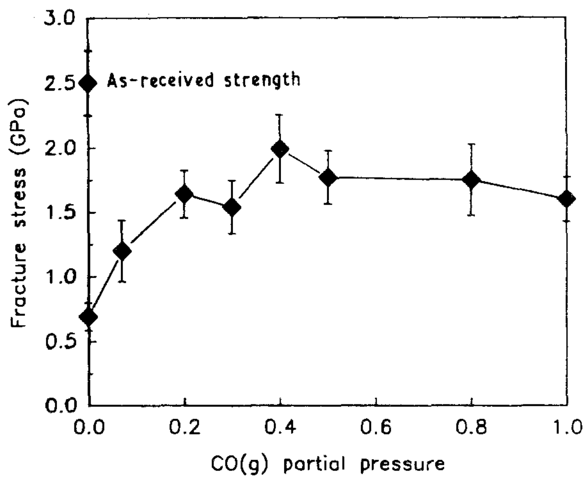

Figure 2 Effect of carbon monoxide partial pressure on fibre strength at 1300 °C, 30 fibres per test condition. Total gas ambient $= p_{CO} + p_{Ar} = 1$ atm.

3.3. SEM analyses

SEM analyses revealed significant differences in the morphology of fibre surfaces with increasing CO(g) partial pressure. The scanning electron micrographs in Figs 3–5 show the most representative features. The fibres heated in 1.0 atm (100%) Ar showed severe surface pitting and porosity (Fig. 3). Similar degradation of fibres heat treated in argon was found by Mah *et al.* [10] and was attributed to the outgassing of fibre decomposition products. The surfaces of fibre specimens heated in the CO/Ar mixtures with less than 0.8 atm CO(g) were smooth and nondescript at the resolution of the SEM (e.g. Fig. 4). When the CO(g) partial pressure was increased to 0.8 and 1.0 atm, roughening and particulates became apparent on the fibre surfaces, as seen in Fig. 5.

TABLE I Tensile strength and per cent strength retention for Nicalon fibres at 1300 °C in various gas mixtures

Partial pressure CO(g)	Number of fibres tested	Tensile strength (GPa)	Standard deviation	Strength retention (%)
As-received	30	2.8	0.8	–
0.0	30	0.7	0.3	27
0.07	30	1.2	0.6	48
0.2	33	1.6	0.5	63
0.3	33	1.5	0.6	59
0.4	32	2.0	0.6	77
0.5	30	1.8	0.6	69
0.8	30	1.8	0.8	69
1.0	32	1.6	0.5	62

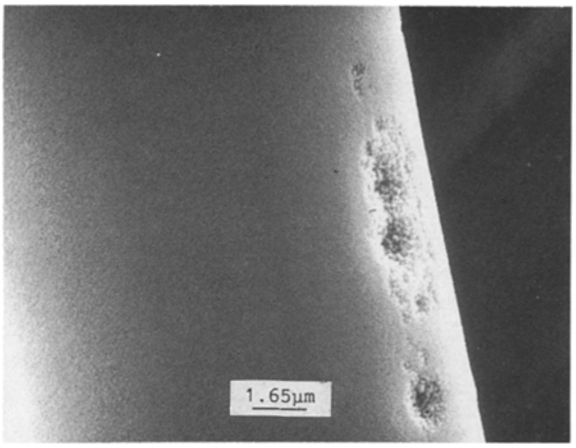

Figure 3 Scanning electron micrograph of fibre surface after 1300 °C heat treatment in 0.0 atm CO (1 atm Ar) for 30 min, showing surface pitting.

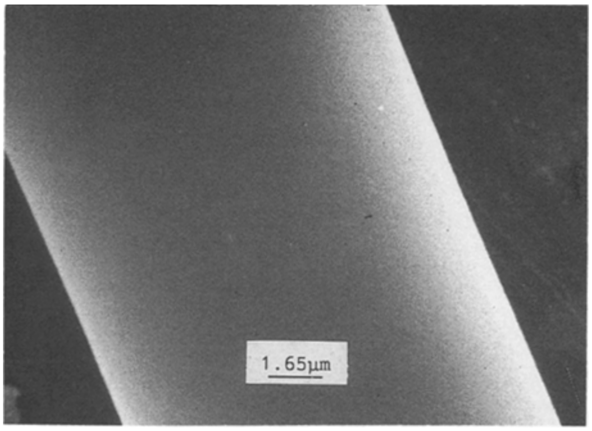

Figure 4 Scanning electron micrograph of smooth fibre surface after 1300 °C heat treatment in 0.4 atm CO for 30 min.

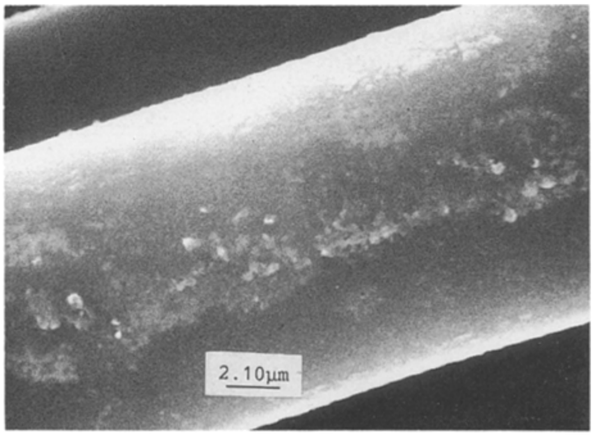

Figure 5 Scanning electron micrograph of roughened fibre surface after 1300 °C heat treatment in 1.0 atm CO for 30 min.

3.4. X-ray diffraction analyses

There was no change in the intensity and shape of the principal characteristic peaks of Nicalon in any of the heat-treated samples. Of particular concern were the presence of peaks due to polymorphs of silica, and any evidence of peak narrowing in the β-SiC which would indicate grain growth. TEM analyses by Bodet [17] and X-ray diffraction by Ishikawa *et al.* [18] support these findings for Nicalon fibres heat treated at 1300 °C for less than 1 h. Thus, grain growth and oxidation which have been determined to be detrimental to the mechanical properties of ceramic fibres can be discounted as significant factors in this investigation.

3.5. Scanning Auger analyses

SAM analyses were performed on selected fibre samples to determine whether composition changes and/or surface reactions occurred as a result of heat treatment. Figs 6–8 present depth profiles of fibres heated in CO partial pressures of 0.0, 0.4, and 1.0 atm, respectively. These profiles show substantial surface and bulk compositional differences between fibres exposed to the different heat-treatment atmospheres. After heat treatment in 1 atm Ar (Fig. 6), an in depth composition change is most apparent. There is a slight amount of oxide on the surface (probably due to the exposure in air after the heat treatment), but primarily, it can be seen that oxygen has been depleted to a depth of at least 100 nm (relative to the initial concentration of 8% O_2). The total depth to which this compositional modification extends is not known.

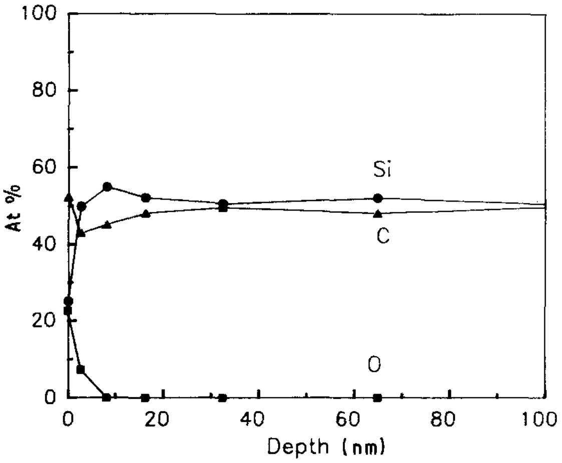

Figure 6 AES depth profile of 0.0 atm CO (1 atm Ar) heat-treated fibre showing carbon and oxygen depletion from the fibre.

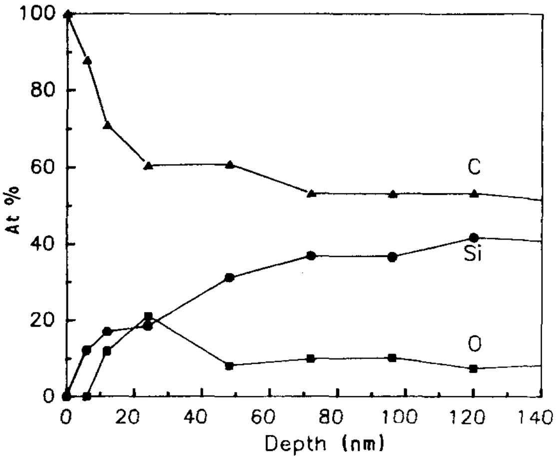

Figure 7 AES depth profile of 0.4 atm CO treated fibre showing a carbon surface layer ~ 15 nm thick.

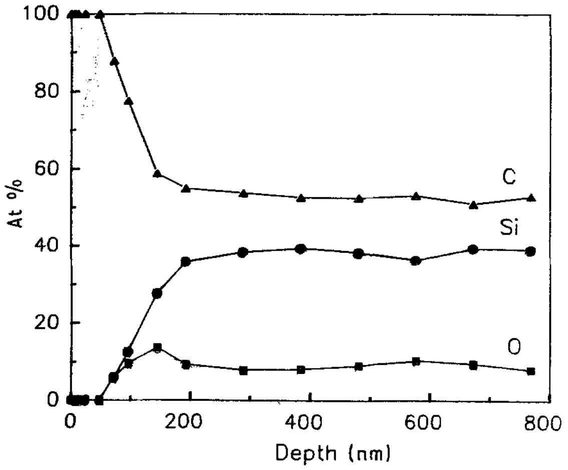

Figure 8 AES depth profile of 1.0 atm CO treated fibre showing a carbon surface layer ~ 60 nm thick.

Conversely, the fibres treated in the CO/Ar mixtures exhibited depth profiles where there was no in-depth depletion of oxygen. Rather, there was a build-up of carbon on the surfaces as shown in Figs 7 and 8. The concentration of carbon increased on the surface with increasing CO(g) activity. In fact, the fibres treated in 0.8 and 1.0 atm CO(g) showed complete coverage of the surface by carbon in the Auger analyses. The depth profiles suggest a layer of carbon on the surface that is about 20 nm thick in the case of 0.8 atm CO(g), and as shown in Fig. 8, is about 60 nm in pure CO(g). It is perhaps most interesting to note that there is a build-up of oxygen at the interface between the carbon surface film and the Nicalon fibre substrate. It is also significant that this sub-surface interface extends some 50–100 nm; i.e. the composition is diffuse over this depth into the Nicalon fibre.

4. Discussion

Obviously, there is no way to be sure that the fibres reached equilibrium after only 30 min at 1300 °C. (The heat-treatment time was intentionally limited to reduce any effects of grain growth). But clearly, the largest decrease in strength was observed when the fibres were heat treated in the absence of CO(g). Moreover, the morphological and compositional analyses indicate that a decomposition reaction had occurred under these conditions. In contrast, there was a limited loss in strength when the fibres were heat treated in CO(g). The fact that a decrease in strength was observed means that certain aspects of the microstructure (i.e. relative phase compositions, grain boundary, and surface energies, etc.) were not in equilibrium. These internal transformations were undoubtedly responsible for the loss in strength observed under these conditions. It is also possible that the generation of SiO(g) was involved in some decomposition of the fibre microstructure. Nonetheless, it can be concluded that the largest contribution to the strength decreases observed in this study were due to the thermochemically driven decomposition reactions that create CO(g).

In the absence of the CO(g) atmosphere, i.e. in the approach to equilibrium, the most important reaction is probably the carbothermal reduction of silica by carbon; namely

$$SiO_2 + 3C \leftrightarrows SiC + 2CO\uparrow \qquad (1)$$

Even if the silica and the carbon in the fibres are associated in an amorphous oxycarbide phase, this decomposition can still be expected; namely

$$SiO_xC_y \rightarrow SiC + C + CO\uparrow \qquad (2)$$

It is probably reactions such as 1 and 2 that are responsible for the loss of oxygen in the fibre surfaces as shown by the Auger analyses. The observed pitting of the fibres may be attributed to the non-uniformity of these reactions in the outermost surface of the fibre.

In the presence of the CO(g) atmosphere, the decomposition reactions that occur to create CO(g) are necessarily limited, especially if the CO(g) pressure is greater than 0.07 atm. Nevertheless, a strength decrease does occur, and moreover, there are changes in the fibre surface composition and morphology. However, it was concluded that the carbon layers that formed on the fibre surface under these conditions were not the result of a surface or in-depth reaction, but rather due to the deposition of carbon via the CO(g) atmosphere

$$2CO \leftrightarrows CO_2 + C \qquad (3)$$

This deposition was verified by repeating some of the experiments in the presence of SiC single crystals. The Auger analyses of these crystals also showed the presence of the carbon layer. This leads to the conclusion that the evolution of CO(g) from the fibres was effectively reduced in these treatments, and therefore, the loss in strength must be attributed to some other change in the microstructure. Although the X-ray analyses failed to detect appreciable grain growth, there may have been limited grain growth which affected the strength of the fibres. In addition, there could have been a change in the phase composition of the fibre, and with it, a change in the microstructure, for example

$$SiO_xC_y \rightarrow SiO_2 + C \qquad (4)$$

The decomposition Reactions 1 and 2 also may play a role in the creation of carbon interphases during the fabrication of Nicalon-reinforced composites. One can only speculate in this case, but it seems well established that the carbon interphase does not form when SiC whiskers or other stoichiometric SiC phases are used; it has been only observed in the case of Nicalon. In this study, it was calculated on the basis of thermochemistry, and shown experimentally, that CO(g) evolution occurs during the heating of Nicalon. This evolution could certainly be expected to occur during the hot-pressing of Nicalon-reinforced glasses and glass-ceramics. Thus the decomposition reaction may be fundamental to the creation of the carbon interphase, and thereby could explain the apparently unique interface reactions in Nicalon-reinforced composites.

5. Conclusions

It was calculated that the thermochemical stability of Nicalon fibres is defined by a reasonably high partial pressure of CO(g); at 1300 °C, this pressure is 0.07 atm. This gas pressure is considered a driving force for the decomposition of Nicalon at elevated temperatures. This hypothesis was tested by heat treating Nicalon fibres at 1300 °C in CO(g) atmospheres. Subsequently, their room-temperature tensile strength was measured, and the fibre surface morphologies and in-depth composition effects were characterized.

It was found that the fibres retained up to 75% of their original strength when heat treated in CO(g) atmospheres, whereas they lost nearly 75% of their strength after heating in argon. The Auger analyses showed an in-depth loss of oxygen and carbon after heat treatment in argon. This is consistent with reactions such as the decomposition of silicon oxycarbide phase, or the carbothermal reduction of residual silica by excess carbon to evolve CO(g). After heat treatment in the CO(g) atmospheres, there was no in-depth composition change observed; in fact, there was a deposition of carbon on the fibre surface.

Although it was already known that decomposition and grain growth limit the high-temperature strength of Nicalon fibres, these experiments have been enlightening. Here, it was shown that the decomposition is specifically associated, to a great extent, with the evolution of CO(g), that there exists a quantitative thermodynamic basis for the reaction and, further, that this decomposition reaction is responsible for most of the strength loss at 1300 °C. It also seems likely that the decomposition reaction may influence the kinetics of grain growth, because it creates gaseous species that can facilitate mass transport. Finally, it was speculated that the decomposition reaction might play a role in the creation of carbon interphases during the hot-pressing of Nicalon-reinforced composites.

Acknowledgements

We gratefully acknowledge the support of ONR contract N00014-90-J-1392 and especially the invaluable Auger analyses provided by J. R. Hoenigman, University of Dayton Research Institute, Dayton, OH.

References

1. K. M. PREWO and J. J. BRENNAN, *J. Mater. Sci.* **15** (1980) 463.
2. R. F. COOPER and K. CHYUNG, *ibid.* **22** (1987) 3148.
3. S. YAJIMA, K. OKAMURA, T. KATSUZANA, Y. HASEGANA and T. SHISHIDO, *Nature* **279** (1979) 706.
4. L. PORTE and A. SARTRE, *J. Mater. Sci.* **24** (1989) 271.
5. C. LAFFON, A. M. FLANK, P. LAGARDE, M. LARIDJAN, R. NAGEGE, P. OLRY, J. COTTERET, J. DIXMIER, J. L. MIQUEL, H. HOMMEL and A. P. LEGRAND, *ibid.* **24** (1989) 1503.
6. Y. SASAKI, Y. NISHINA, M. SATO and K. OKAMURA, *ibid.* **22** (1987) 443.
7. B. CATOIRE, M. SOTTON, G. SIMON and A. R. BUNSELL, *Polymer* **28** (1987) 751.
8. T. S. CLARK, M. JAFFE, J. RABE and N. LANGLEY, *Ceram. Engng. Sci. Proc.* **7** (1988) 901.
9. T. S. CLARK, R. M. ARONS, J. B. STAMATOFF and J. RABE, *ibid.* **6** (1985) 576.
10. T. MAH, N. L. HECHT, D. E. McCULLUM, J. R. HOENIGMAN, H. M. KIM, A. P. KATZ and H. A. LIPSITT, *J. Mater. Sci.* **19** (1984) 1191.
11. J. J. CLARK, E. R. PRACK, M. I. HAIDER and L. C. SAWYER, *Ceram. Engng Sci. Proc.* **8** (1987) 717.
12. D. J. PYSHER, K. C. GORETTA, R. S. HODDER Jr and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **72** (1989) 284.
13. K. L. LUTHRA, *ibid.* **69** (1986) C231.
14. S. M. JOHNSON, R. D. BRITTAIN and R. H. LAMOREAUX, "Degradation of SiC Fibres", in "High Temperature Materials Chemistry IV", edited by Z. A. Munir, D. Cubicciotti and H. Tagawa (The Electrochemical Society, Pennington, NJ, 1988) pp. 355–61.
15. S. M. JOHNSON, R. D. BRITTAIN, R. H. LAMOREAUX and D. J. ROWCLIFFE, *J. Amer. Ceram. Soc.* **71** (1988) C132.
16. J. LIPOWITZ, G. LeGROW, T. LIM and N. LANGLEY, *Ceram. Engng Sci. Proc.* **9** (1988) 931.
17. R. BODET, private communication, The Pennsylvania State University (1990).
18. T. ISHIKAWA, H. ISHIKANA and H. TERANISHI, "Strength and Structure of SiC Fiber After Exposure to High Temperature", in "High Temperature Materials Chemistry IV", edited by Z. A. Munir, D. Cubicciotti and H. Tagawa (The Electrochemical Society, Pennington, NJ, 1988) pp. 205–11.
19. A. G. EVANS, *J. Amer. Ceram. Soc.* **73** (1990) 187.
20. G. ERIKSSON, *Chem. Scripta* **8** (1975) 100.
21. "JANAF Thermochemical Tables", 3rd Edn, NSRDS-BS 37 (1986).
22. I. BARIN and O. KNACKE, "Thermochemical Properties of Inorganic Substances" (Springer-Verlag, New York, 1973).
23. P. M. BENSON, K. E. SPEAR and C. G. PANTANO, "Thermochemical Analyses of Interface Reactions in Carbon-Fiber Reinforced Glass Matrix Composites, in "Ceramic Microstructures '86", edited by J. A. Pask and A. G. Evans (Plenum Press, New York, 1987) pp. 415–25.

Received 25 July
and accepted 20 December 1990