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Creep behaviour and structural characterization at high temperatures of Nicalon SiC fibres

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Two types of Nicalon SiC fibres having different structures have been examined. Their mechanical properties and their microstructures have been studied up to 1300° C. The fall in strength above 1000° C has been shown to be due to the microcrystallization of the fibre structure. Under low loads this change in structure led to a shrinkage of the fibre. The fibres were found to creep at temperatures above 1000° C when loads greater than a threshold level were applied. The creep of the fibres has been shown to be controlled by the changes which occur to the fibre structure. Degradation of the fibres on heating in air or argon has been shown to depend on SiO_2 and free carbon, which have been shown to exist in the fibre.

1. Introduction

The simple tensile properties of Nicalon SiC fibres up to 1300° C as well as their initial microstructure have been described in an earlier publication [1]. Two types of Nicalon SiC fibres were tested, identified as NLP 101 and NLM 102. The former was shown to be amorphous whilst the latter was microcrystalline with a grain size of about 1.7 nm. Both fibres were found to consist of SiC with an excess of carbon and SiO_2. The NLM 102 fibre contained twice as much carbon as did the NLP 101 fibre. The carbon was segregated into clusters of about 2.0 nm radius in the NLP 101 fibre whereas two populations existed for the NLM 102 fibre of 1.5 and 2.2 nm radii. The strengths of both fibres were found to fall above 1000° C. An analysis of loads at failure based on Weibull statistics revealed that heating the NLP 101 fibre in air above 1000° C produced new types of defect in the fibre whereas this was not so when it was heated in argon or when the NLM 102 fibre was

The present paper examines more closely the mechanical behaviour of these two fibres above 1000° C as well as their structural modifications at high temperatures.

2. Experimental details

The experimental techniques used in this study have been described elsewhere [1]. The mechanical testing was conducted on a Universal Fibre Tester to which had been added a furnace enabling tests on single fibres to be made up to 1600° C. The size of the furnace meant that long specimens (220 mm) only were tested. The grips in which the fibre was held were maintained at 24° C and the temperature gradients inside the furnace are shown in Fig. 1 for tests at 1300° C. As the mechanical properties of the fibre had been found not to vary greatly up to 1000° C the length subjected to the test temperature was approximated to that length of furnace over 1000° C.

Structural analysis was performed using transmission electron microscopy, electron microprobe, X-ray diffraction and electron spin resonance (ESR). This latter technique permitted the evolution and importance of the excess carbon to be evaluated at high temperature. Specimens for the ESR analysis were prepared by grinding the fibres and mixing the particles with silica gel powder.

3. Results

3.1 Creep tests on the NLP 101 fibres

No creep of the NLP 101 fibres was detected up to 1000° C at which temperature the strain rate was found to be less than $10^{-8}\,\text{sec}^{-1}$ for an applied stress of 0.9 GPa. Above this temperature the fibre

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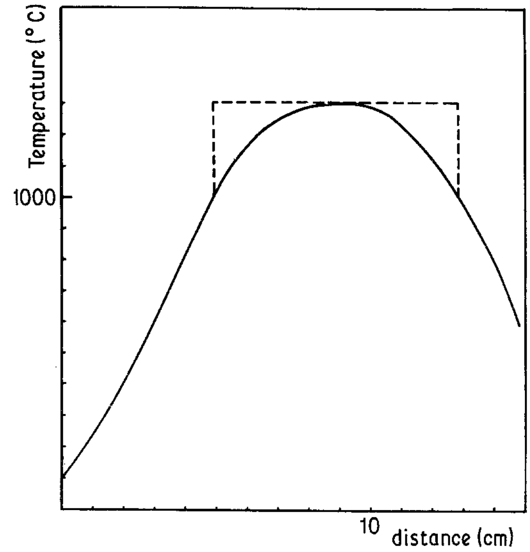

Figure 1 Temperature gradient in the furnace for tests at 1300° C.

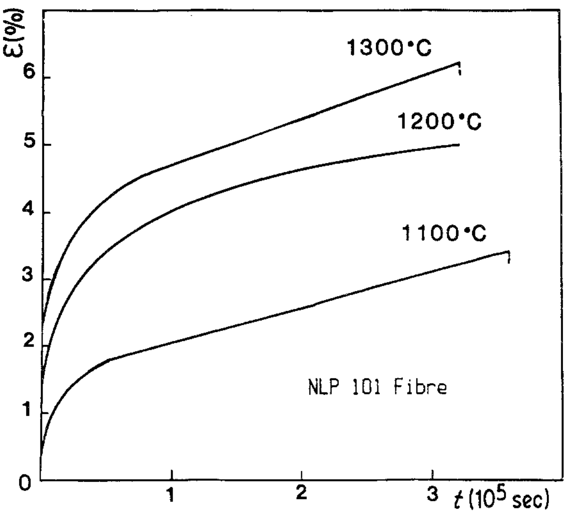

Figure 2 Mean creep curves in argon atmosphere; stress 0.6 GPa.

strength fell and creep became discernible. The temperature range examined, therefore, was 1000 to 1300° C above which the fibre strength was very low. The loading range was 0.05 to 0.8 GPa. Tests were conducted in air and argon and were limited to 100 h whether failure had or had not occurred. The mean strength of the fibres at 1300° C was about 0.5 GPa so that some fibres did not survive the initial loading to 0.8 GPa. The scatter in lifetimes to failure was therefore wide and it was considered that little significance could be drawn from lifetime measurements.

Fig. 2 shows the average creep curves, at each temperature, for an applied stress of 0.6 GPa. Figs. 2 and 3 show that the creep was initially logarithmic at 1100 and 1300° C and then followed by linear behaviour. At 1200° C the creep remained logarithmic for about 70 h after which it became almost imperceptible.

At small applied stresses (0.05 GPa) the fibre was found to shrink and this phenomenon increased with temperature attaining 1% at 1300° C. Shrinkage stopped after several hours.

A stress threshold level was found to exist up to 1200° C, below which creep did not occur. This was not found at 1300° C.

It became clear from these results several mechanisms were active in the temperature range studied so that the creep activation energy, ΔH, was not calculated as the gradient of log $\dot{\epsilon}$ as a function of the reciprocal of the temperature. A measure of the activation energy was made by varying the temperature during a creep test at constant applied stress around the temperature considered.

At 1100° C the stress threshold above which creep was observed was 0.3 GPa. The constant creep rate ($\dot{\epsilon}$) obeyed the relation:

$$\dot{\epsilon} = A(\sigma - \sigma_0)^n \exp(-\Delta H/RT), \qquad (1)$$

where σ was the applied stress, σ_0 the stress threshold, ΔH the activation energy, R the gas constant, T the absolute temperature, and A a constant.

The value of m was calculated from the gradient of the curve of log $\dot{\epsilon}$ as a function of log σ. The

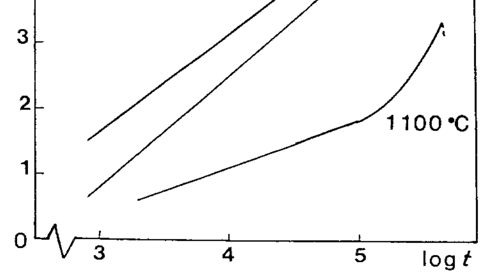

Figure 3 Mean creep curves; logarithmic time scale.

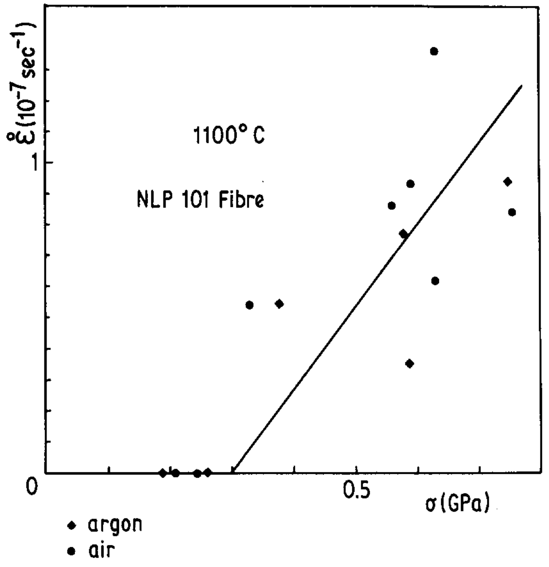

Figure 4 Dependence of the strain rate on stress at 1100° C.

value of n was found to be almost unity (0.97). There were no differences observed between the creep of the fibres in air and that in argon, as shown in Fig. 4.

The activation energy was determined from the differences in strain rate measured at 1080 and 1120° C during a test at 0.6 GPa. Its value was found to be $\Delta H = 490\,\text{kJ mol}^{-1}$.

At 1200° C the creep stress threshold level was at 0.17 GPa. Above this stress the strain rate was not constant but a graph of $\dot{\epsilon}$ as a function of time showed a pseudo linear part. In order to compare results at different applied stresses it was arbitrarily chosen to compare the values of the strain rate after 10^5 sec which fell within the pseudo linear range of the curves.

The value of n in Equation 1 was found to be 1.9 and, as Fig. 5 shows, no effect of the atmosphere was seen. A variation of temperature from 1180 to 1220° C gave an activation energy of $380\,\text{kJ mol}^{-1}$,

At 1300° C there was no indication of a creep stress threshold level even at stresses as low as 0.1 GPa. Fig. 6 shows that different results were obtained in the two atmospheres. Creep in air was at a lower rate than in argon and the values of n were different with $n = 1.1$ in air and $n = 1.9$ in argon.

The activation energies in each environment were found by varying the temperature from 1280 to 1320° C and gave values of $270\,\text{kJ mol}^{-1}$ in air and $370\,\text{kJ mol}^{-1}$ in argon.

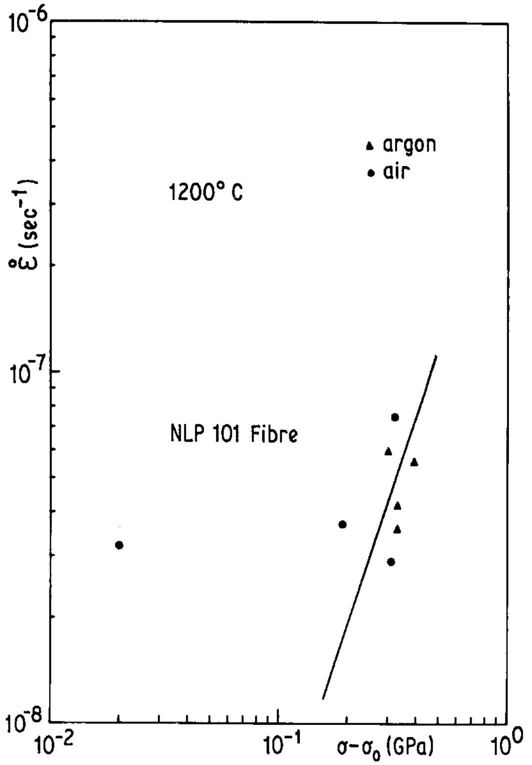

Figure 5 Dependence of the strain rate on stress at 1200° C. $t = 10^5$ sec, $\sigma_0 = 0.17$ GPa.

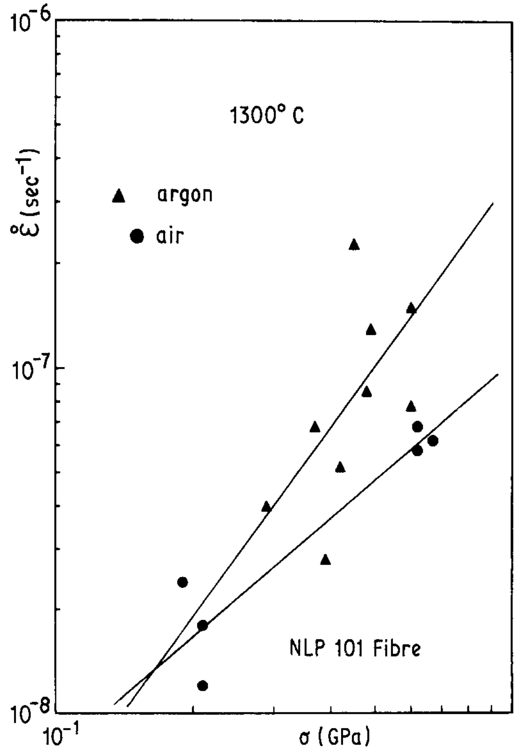

Figure 6 Dependence of the strain rate on stress at 1300° C.

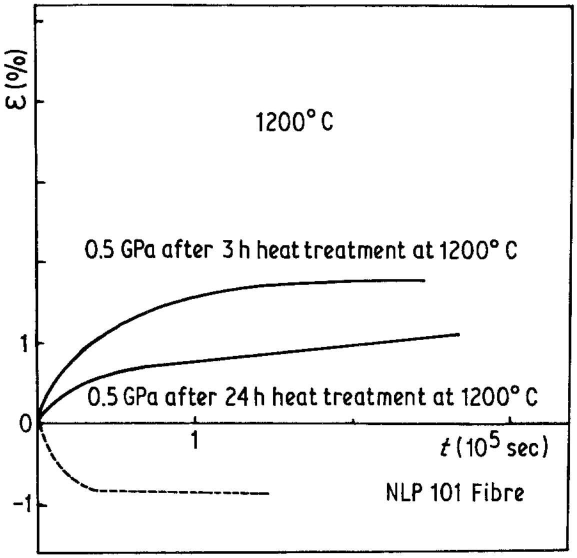

Figure 7 Influence of annealing on creep curves at 1200° C (dotted line: shrinking at 1200° C and 50 MPa).

3.2. Creep after heat treatment

The creep behaviour of NLP 101 fibres observed at 1200 and 1300° C suggested that the microstructure of the fibre was being modified with a stable state being attained quicker at the higher temperature. The fibres were therefore heat treated before testing in order to examine the effect of the treatment on creep behaviour. The heat treatment took place with the fibre mounted in the Universal Fibre Tester and subjected to a steady load of 1 g (about 0.05 GPa).

At 1200° C in an argon atmosphere and under a steady applied stress of 0.1 GPa, a shrinkage was observed to occur for approximately 20 h after which no further change was seen, as is shown in Fig. 7. After heat treatment lasting 3 h, the creep curve obtained with an applied stress of 0.5 GPa revealed that complete stabilization of the structure had not occurred. The creep behaviour was still logarithmic; however, the primary creep had decreased notably. The creep rate after 10^5 sec was found to be unchanged when compared to the non-heat-treated fibre. After 24 h treatment, primary creep ceased after less than 10 h and the secondary creep was linear.

At 1300° C shrinkage under low load (0.05 GPa) was seen to stop after 3 h. Creep tests after heat treatment for 3 h showed reduced primary creep, as shown in Fig. 8, and very little effect on the secondary creep (see Fig. 9).

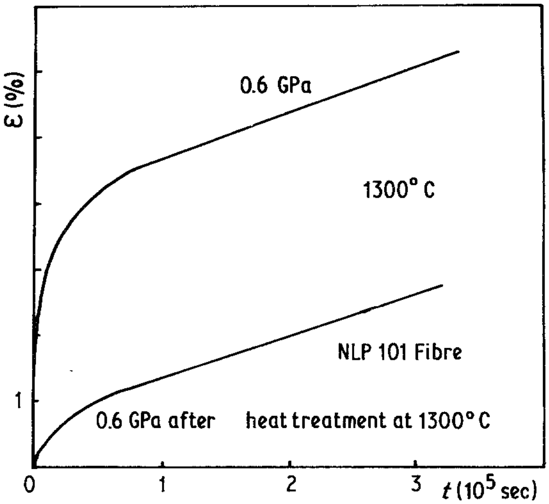

Figure 8 Influence of annealing on creep curves at 1300° C.

3.3. Comparison of the behaviour of the NLP 101 and NLM 102 Nicalon fibres

The differences of microstructure observed between the two fibres was expected to lead to different creep behaviours [1]. The NLM 102 fibre was found to show less primary creep so that at 1300° C under 0.6 GPa applied stress the strain at the end of the primary creep was around 1% as compared to 4 to 5% for the NLP 101 fibre. However, the NLM 102 fibre was found to fail more quickly than the NLP 101 fibre under the same applied stress of 0.6 GPa; so much so that it was difficult to reach to reach the domain of secondary creep.

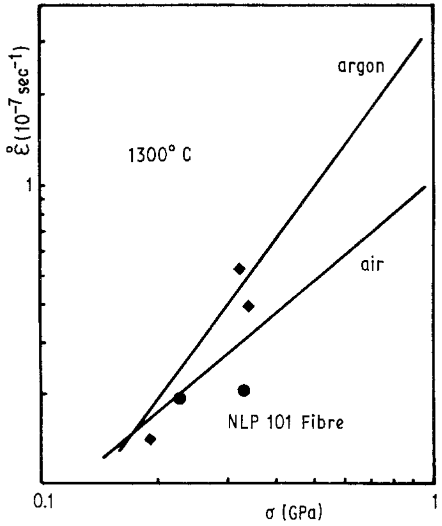

Figure 9 Secondary creep rate is not influenced by heat treatment at 1300° C.

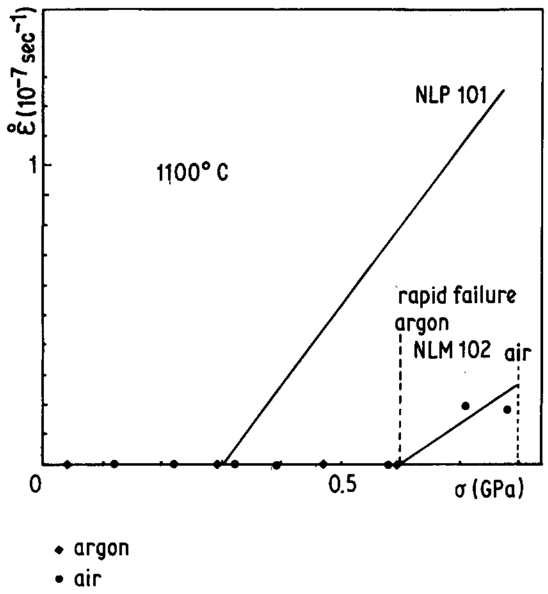

Figure 10 Dependence of the strain rate on stress at 1100° C, type NLM 102.

The secondary creep rate was, however, seen to be less with the NLM 102 fibres. No creep stress threshold was observed at 1300° C although a threshold of 0.15 GPa was observed at 1300° C for the NLM 102 fibres tested in air. Unlike the behaviour of the NLP 101 fibres the NLM 102 fibres showed linear secondary creep behaviour at 1200° C.

At 1100° C the creep threshold stress of the NLM 102 fibres was 0.6 GPa. These fibres were found to be rapidly damaged in an argon atmosphere. In air the NLM 102 fibre showed longer lifetimes, and between 0.6 and 0.8 GPa linear secondary creep was seen attaining very low strain rates. Above 0.8 GPa the fibre failed very quickly. The results for both fibres are shown in Fig. 10.

At 1200° C the creep stress threshold was either non-existent or very low ($\sigma_0 < 0.1$ GPa). Fig. 11 shows the creep rate of the NLM 102 fibres as a function of applied stress. It can be seen to be lower than for the NLP 101 fibre.

At 1300° C the creep stress threshold was around 0.2 GPa in air and in argon the creep rate was very low under low stresses, as can be seen from Fig. 12. The secondary creep rate was seen to be lower than that in air as was seen with the NLP 101 fibre. It was not possible to conduct creep tests with the NLM 102 fibre over 0.55 GPa as failure occurred too rapidly.

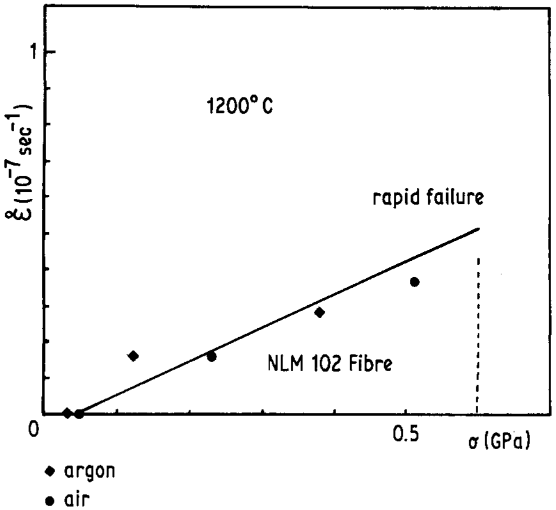

Figure 11 Dependence of the strain rate on stress at 1200° C, type NLM 102.

3.4. Electron microprobe analysis of the oxidation of the SiC

The variation of oxygen content across the NLP 101 fibre diameter after 1 h of heat treatment was determined by X-ray diffraction. Fig. 13 shows that no surface oxide layer was created at 1100° C but that one appeared at 1200° C with a thickness of about 0.5 μm and it became more predominant at 1300° C with a thickness of about

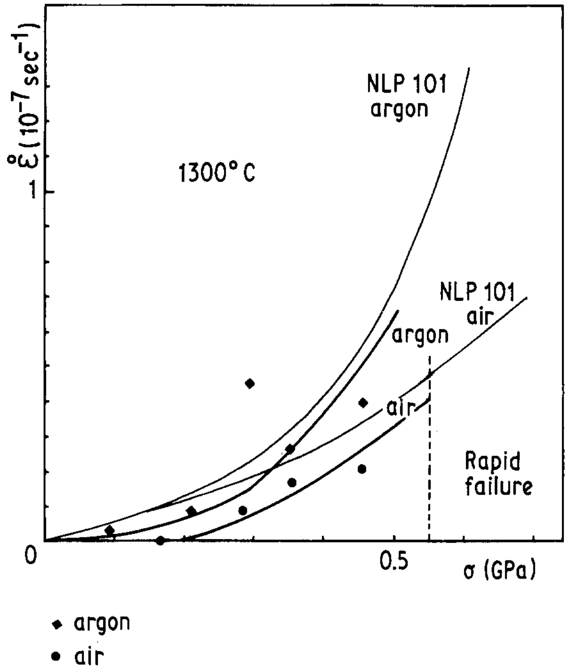

Figure 12 Dependence of the strain rate on stress at 1300° C, type NLM 102.

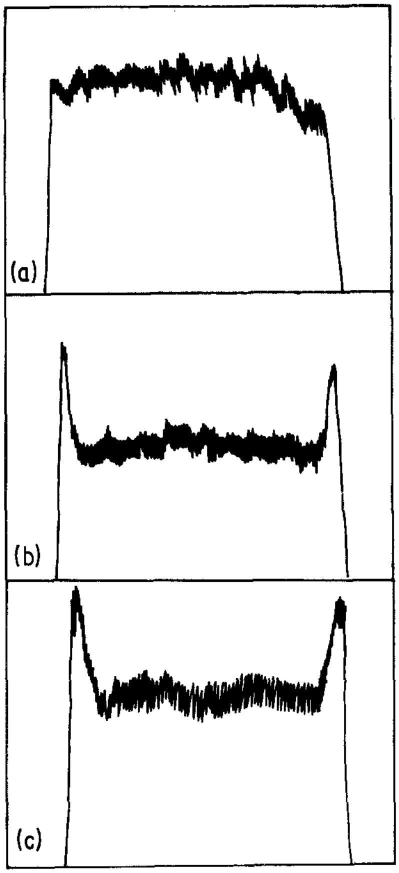

Figure 13 Evolution of the oxygen concentration profile in the NLP 101 fibre after 1 h annealing in air at 1100, 1200 and 1300° C.

0.8 μm. A thin oxide coating may have existed at 1100° C which could not be detected because of the limitations of the technique.

3.5. X-ray diffraction studies of the crystallization of SiC

It has previously been shown that the microstructure of the NPL 101 fibre was amorphous. The X-ray diffraction peak was seen to reduce in width up to 1200° C indicating an increase in ordering of the fibre structure which, however, was still considered to be amorphous. After 1 h in air at 1300° C the NPL 101 fibre was seen to contain small crystals of β-SiC. Fig. 14a shows the mean size of SiC grains after 1 h thermal treatment at different temperatures and Fig. 14b shows growth of grain size with time at 1300° C. The grains of SiC quickly stabilize at a size of about 3.0 nm.

Figs. 15a and b show the results for the NLM 102 fibre subjected to heat treatment. It can be seen that in the temperature range studied the structure again stabilizes with a SiC β grain size of about 3.0 nm. Stability of the structure is reached in about 5 h at 1300° C and 20 h at 1200° C.

3.6. Transmission electron microscopy analysis

This technique has only been used to study the NPL 101 fibres having undergone heat treatment at 1200 and 1300° C and creep at 1100, 1200 and 1300° C.

At 1100° C a study was made of fibres having been subjected to creep for 22, 45 and 60 h in air and in argon. The diffraction patterns and dark-field micrographs corresponding to the first diffraction ring are shown in Figs. 16a, b and c. It is clear from these figures that there was no change of the fibre structure and it remained amorphous throughout the creep test of 100 h.

At 1200° C the structure of the fibre after 2 h under low load (0.05 GPa) was seen to remain amorphous, as can be seen from Fig. 17. The X-ray diffraction studies had shown that 20 h of treatment were necessary for crystallization to occur. Under creep conditions at 1200° C the structural changes in the NLP 101 fibre were different from that seen during heat treatment. After 22 h the structure was still amorphous as shown by Fig. 18a, and after 31 h the structure was still glass like containing a few small crystals, as shown in Fig. 18b. At 50 h, Fig. 18c shows that the fibre structure had become crystalline.

At 1300° C the same scenario as was seen at 1200° C was repeated but the metamorphosis was quicker. After 3 h at 0.05 GPa the fibre was crystalline, as can be seen from Fig. 19, and which confirms the results obtained by X-ray diffraction. However, the size of the crystals was observed to be only 1.8 nm and not 3.0 nm as given by the Scherrer formula for X-ray diffraction. The rate of crystallization during creep was again observed to be slower than during the heat treatment, as illustrated by Fig. 20. After 6 h at 1300° C with 0.6 GPa applied stress, the NPL 101 fibre was still amorphous, and only after 13 h was it crystalline. It was necessary, however, to continue the creep test for 31 h before a densely packed crystalline structure was obtained with a grain size of 3.0 nm, as can be seen from Fig. 21a. Thereafter the grain size was not observed to increase and the structure appeared stable (see Fig. 21b). No difference was found whether the fibre was heated in air or argon.

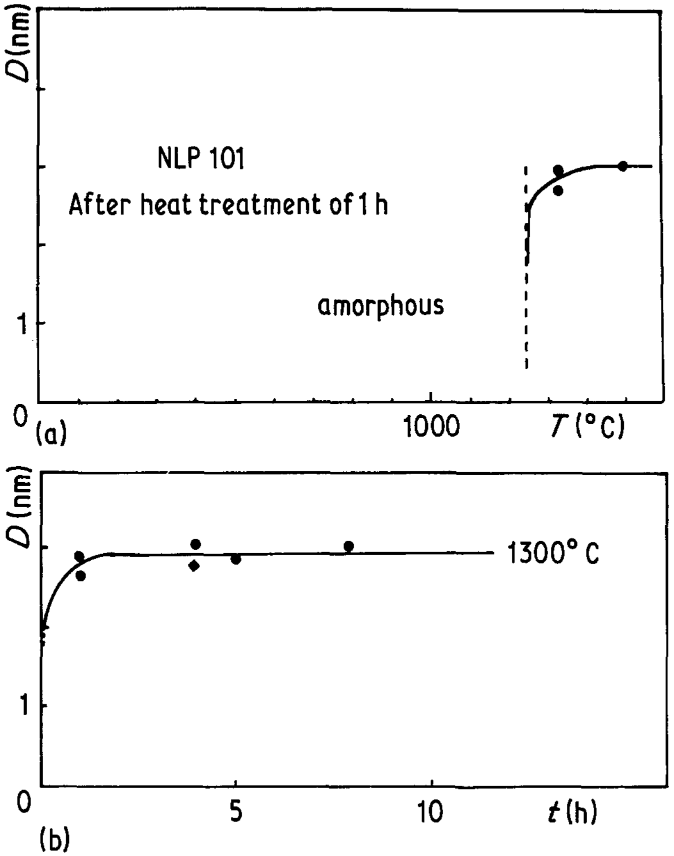

Figure 14 Mean size of SiC β cristals (Scherrer analysis of X-ray diffraction profiles) for NLP 101 fibre as a function of (a) heat-treatment temperature (1 h); (b) time of heat treatment at 1300° C.

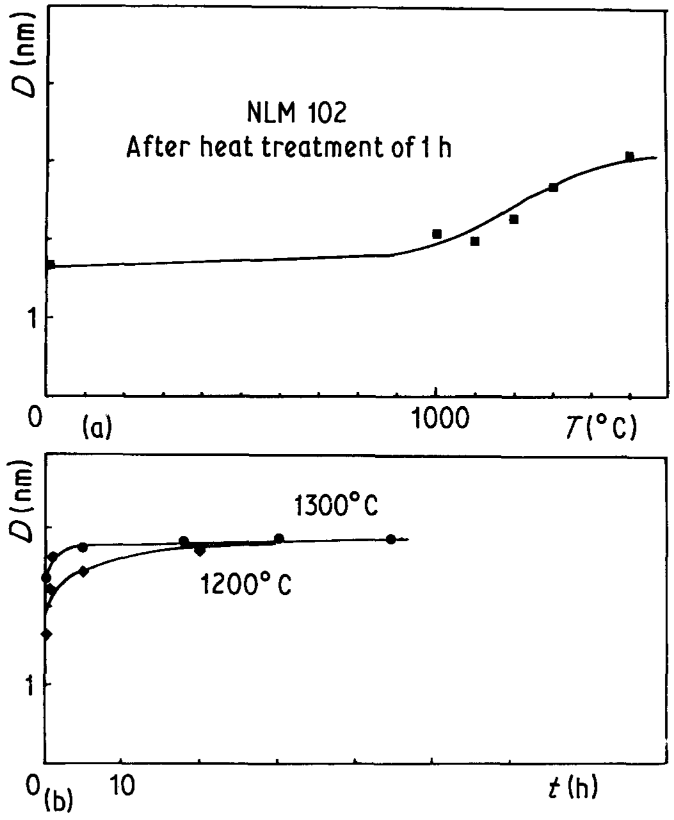

Figure 15 Mean size of SiC β crystals for NLM 102 fibre as a function of (a) heat-treatment temperature (1 h); (b) time of heat treatment at 1200 and 1300° C.

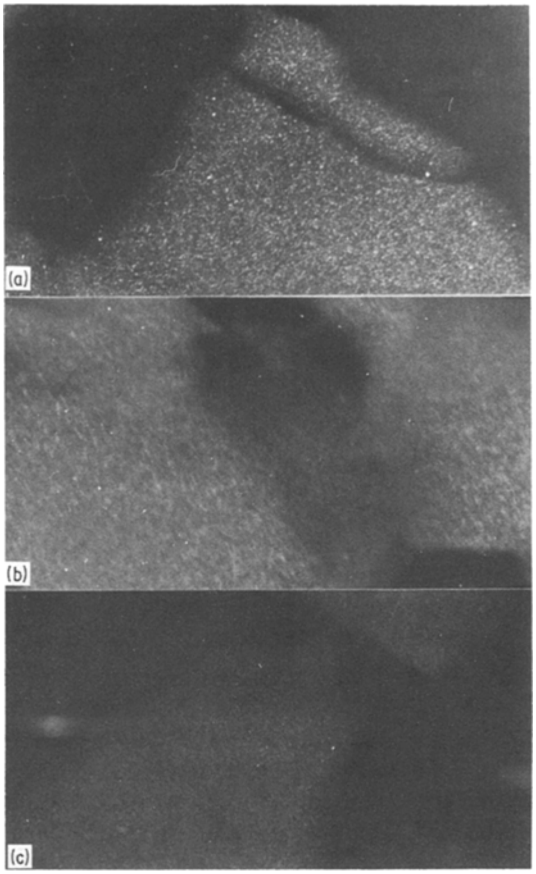

Figure 16 Dark-field image of NLP 101 fibre after creep at 1100° C and 0.6 GPa in an argon atmosphere, (a) for 22 h, (b) for 45 h, (c) for 60 h. The structure remains amorphous.

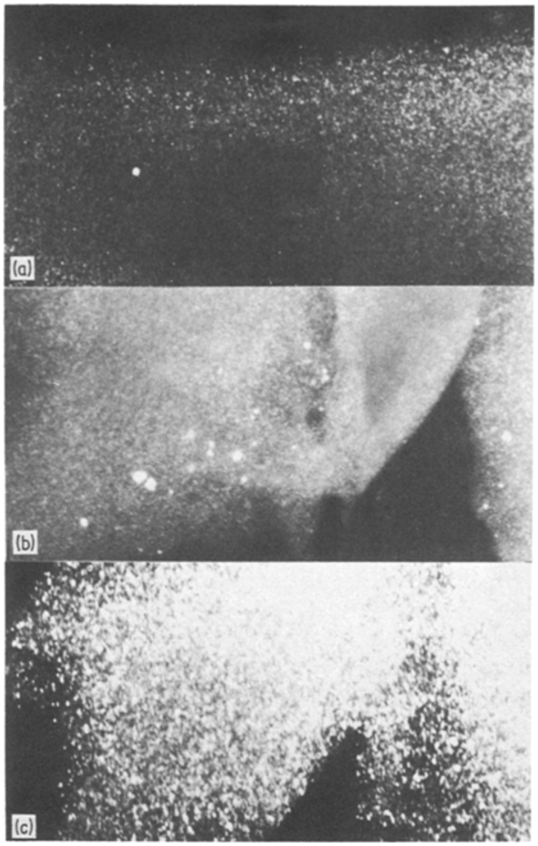

Figure 18 Dark-field image of the NLP 101 fibre after creep at 1200° C and 0.6 GPa in an argon atmosphere. (a) 22 h, (b) 31 h, (c) 50 h. Slow crystallization, Average grain size is 3 nm when equilibrium is reached.

The rates of crystal growth during creep at 1200 and 1300° C with 0.6 GPa applied stress are shown in Fig. 22. It can be seen that the structure was found to stabilize at 1300° C after 20 h and after 50 h at 1200° C. These results are strikingly different when compared to the stabilization which occurred during heat treatment, 5 h at 1300° C and 20 h at 1200° C.

3.7. Electron spin resonance (ESR)

This technique was employed in order to study

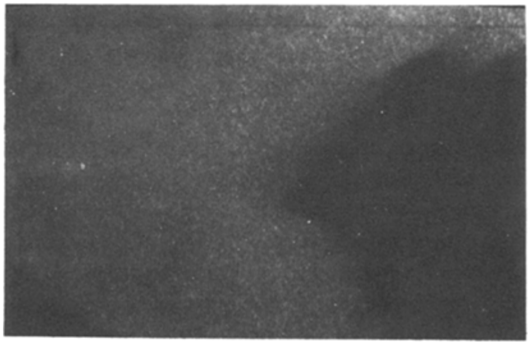

Figure 17 Dark-field image after 3 h heat treatment of the NLP 101 fibre at 1200° C in an argon atmosphere. The structure remains amorphous.

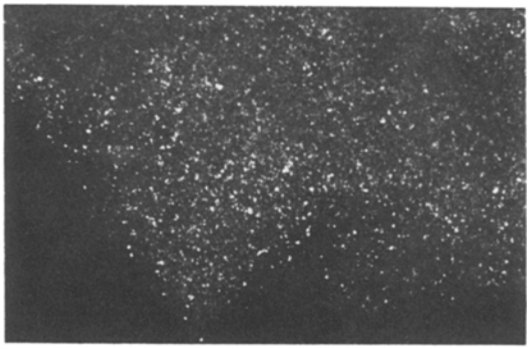

Figure 19 Dark-field image after 3 h heat treatment of the NLP 101 fibre at 1300° C in an argon atmosphere. Mean grain size 1.8 nm.

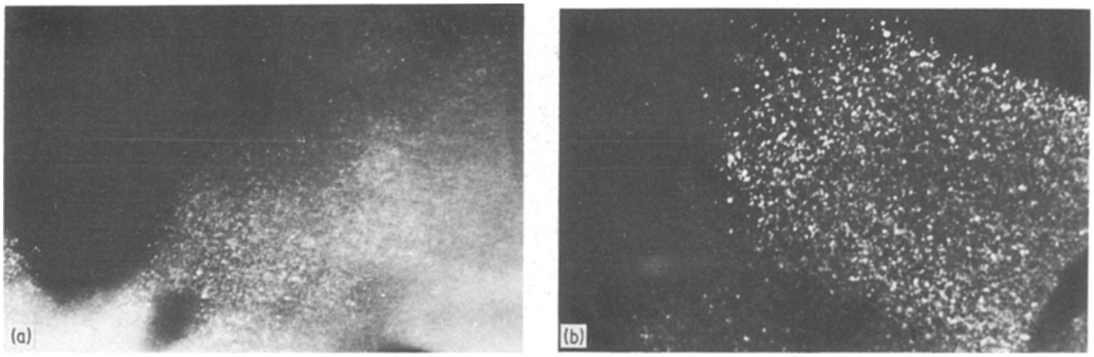

Figure 20 Dark-field image of the NLP 101 fibre after creep at 1300° C and 0.6 GPa in an argon atmosphere. (a) 6 h, the structure is amorphous. (b) 13 h, mean crystal size 1.8 nm.

the evolution of the free carbon segregates during various heat treatments. The study was conducted with the NLM 102 fibre as it contained the greater amount of free carbon. The heat treatments applied were between 1000 and 1500° C in both air and argon and at 1900° C in an atmosphere of argon containing extremely little oxygen. Fig. 23 shows a comparison of the ESR spectra for both fibres plotted as the ESR intensity as a function of free carbon content measured by Auger spectrometry [1]. In this way the intensity of the ESR as a function of free carbon content could be calibrated. Fig. 24 shows the intensity of the ESR after 1 h heat treatment in air and argon. The reactivity of the free carbon was seen to be greater in the argon atmosphere than in air and at 1900° C all of the free carbon had disappeared. The reactivity of the free carbon as a function of time at 1300° C in air, just under the temperature at which the reactivity had been seen to increase dramatically, is shown in Fig. 25. It can be seen that the intensity of the ESR stabilized after 5 h at 1300° C at a level corresponding to 15 mol %. In argon the free carbon falls and stabilizes after 1 h at 1300° C at a level of 5 mol %.

4. Discussion

The shrinkage of the fibres observed during heat treatment at 1200 and 1300° C can be explained by changes of the structure: crystallization in the case of the NLP 101 fibres and recrystallization in the case of the NLM 102 fibres. The fibres did not shrink at 1100° C. No change in fibres structures was found at 1100° C whereas a gradual evolution occurred at 1200° C and rapid stabilization at 1300° C. Equilibrium was reached after 20 h at 1200° C and 5 h at 1300° C after which time the SiC grain size was 3.0 nm.

The amount of free carbon decreased rapidly during heat treatment in air but was quicker and more complete in argon. This was probably due to a reaction of the carbon with the SiO_2 which is present throughout the fibre structure [1]. This reaction was probably slower in air because it is known that the creation of a film of SiO_2 at the fibre surface would inhibit the diffusion of CO caused by the reduction of the silicon oxide in the bulk of the fibre [2].

The fibre structure was found to evolve rather differently during creep. This was determined by using transmission electron microscopy which

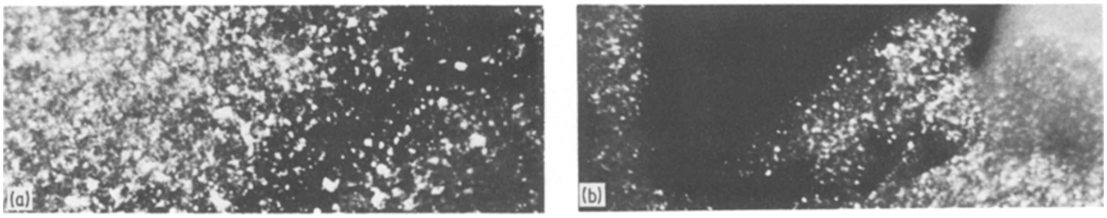

Figure 21 Dark-field image of the NLP 101 fibre after creep at 1300° C and 0.6 GPa in an argon atmosphere. (a) 31 h, (b) 65 h. The grain size stabilizes at 3 nm.

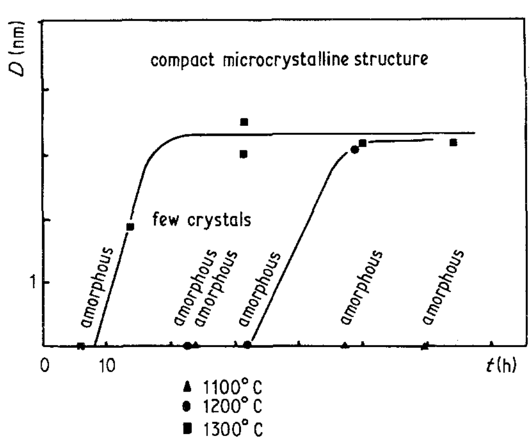

Figure 22 Dependence of the mean grain size on time during creep at 0.6 GPa.

enabled the growth of the SiC crystals to be observed and measured. It was assumed that the SiO_2 and free carbon content varied as had been observed during heat treatment, as the electron microscope could give no information on that point. It was observed that the fibres under load crystallized more slowly than when under no load, 20 h at 1300° C and more than 50 h at 1200° C with a final SiC grain size of 3.0 nm.

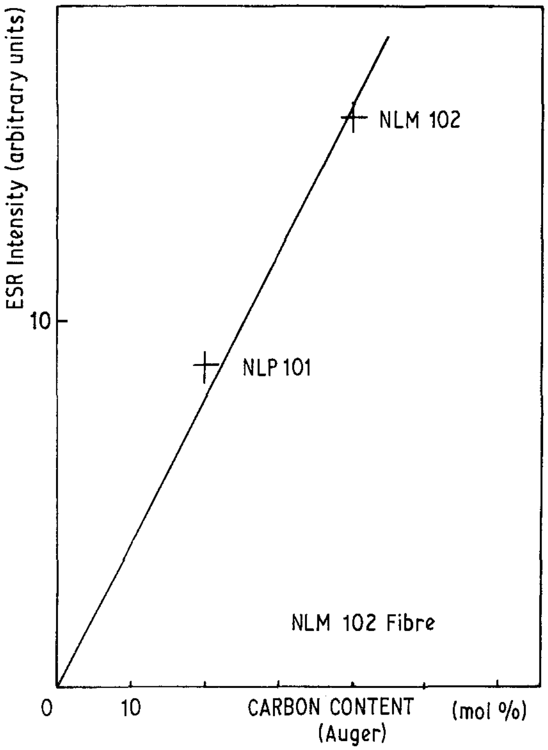

Figure 23 ESR intensity as a function of the percentage of free carbon calibrated by Auger spectroscopy.

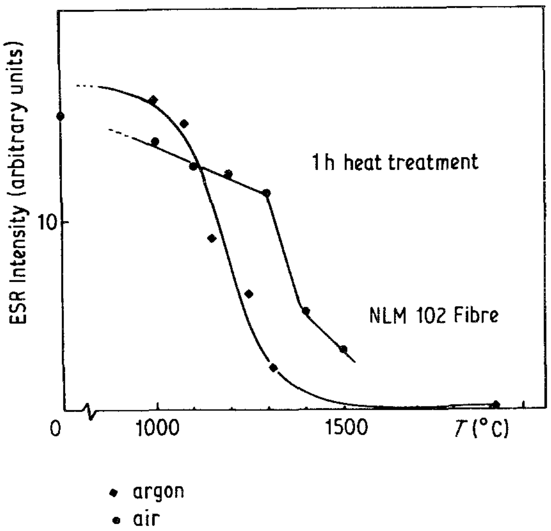

Figure 24 Dependence of ESR intensity on heat-treatment temperature (1 h).

No structural modification was seen during creep at 1100° C; however, at 1300° C the observation that secondary creep occurred only after the structure had reached equilibrium supports the Ashby–Verrall model for creep deformation in which there is no elongation of the grains [3].

The existence of creep stress threshold levels up to 1200° C for the NPL 101 fibre indicates the existence of a distribution of particles blocking deformation [4]. The analyses by ESR and X-ray scattering [1] have shown that these particles are grains of carbon of about 2.0 nm radius embedded in the matrix of SiC and SiO_2. The stress threshold level was found to decrease with temperature (0.3 GPa at 1100° C and 0.17

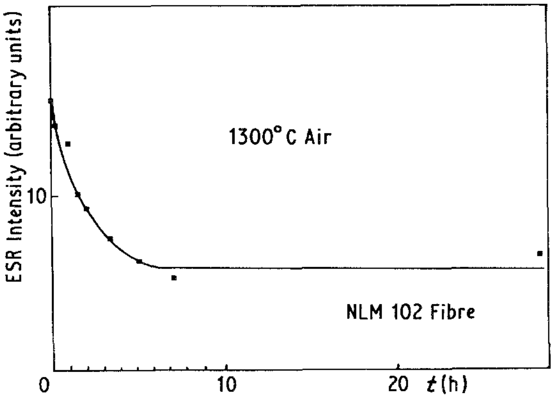

Figure 25 Dependence of ESR intensity on heat-treatment time at 1300° C in air.

GPa at 1200° C) and probably corresponds to a decrease in free carbon as shown by ESR to occur in the NLM 102 fibre. The NLP 101 fibre contains approximately half the free carbon and more SiO_2 than is in the NLM 102 fibre. It seems reasonable to suppose that the free carbon content of the NLP 101 fibre is very small after the 20 h primary creep at 1300° C.

At 1100° C the activation energy for the NLP 101 fibre was 490 kJ mol^{-1}. The structure was observed to be amorphous so that diffusion along grain boundaries was not possible but nevertheless this value of ΔH is less than that measured for carbon in a monocrystal of SiC [5]. This is no doubt due to the more open structure of an amorphous arrangement.

The creep rate for NLP 101 fibres at 1200° C was seen to decrease and this has been shown to be due to a slow crystallization of the structure which takes about 50 h.

At 1300° C the fibre structure reaches an equilibrium with a mean SiC grain size of 3.0 nm after 20 h which corresponds exactly to the end of the primary creep phase. The structure remains stable during secondary creep which suggests that it is must be due to slippage and diffusion as described by Ashby and Verrall [3]. This mechanism would be independent of the atmosphere in which the fibre was heated; however, a difference was seen between the behaviours in air and argon. Creep at 1200° C in air and in argon as well as at 1300° C in argon revealed the same values for n and ΔH (2 and 370 kJ mol^{-2}) suggesting that under these conditions the creep processes were common.

The NLM 102 fibre was found to creep less than the NLP 101 fibre and this seems to be related to its structure being already microcrystalline and denser. At 1100° C the creep stress threshold is very high (0.6 GPa) and this is probably due to the high free carbon content (40 mol% compared to 20 mol% for the NLP 101 fibre) which prevents creep. The mean lifetimes of NLM 102 fibres were shorter in an argon atmosphere than in air as in the latter case the reaction C/SiO_2 is inhibited. This observation suggests that the lifetime is related to the speed of this reaction which must result in serious degradation of the fibre. As the NLM 102 fibre contains more free carbon than the NLP 101 fibre, this results in it having shorter lifetimes under all the conditions where creep occurs.

At 1200° C the NLM 102 fibre showed normal linear secondary creep unlike the NLP 101 fibre. This was due to the NLM 102 fibre having an initial microcrystalline structure whereas the NLP 101 passed through a long stage of slow crystallization. No creep threshold level was observed at 1200° C for the NLM 102 fibre, despite there still being free carbon in its structure. It must be supposed that this slowed down the creep but did not halt it completely. At 1300° C a creep threshold limit was observed in air but not in argon, which again is explained by there remaining free carbon segregates in air whereas they had disappeared in argon. This may also explain the differences of creep rate seen in air and argon.

No immediate explanation comes to mind to explain why there is no creep stress limit at 1200° C and that the creep rate was higher than at 1300° C at low stresses.

The short lifetimes of the NLM 102 fibre at 1300° C with applied stress greater than 0.5 GPa is again explained by the degradation due to the C/SiO_2 reaction.

5. The optimum fibre structure for use above 1000° C

This study has been concerned with two fibres produced in similar ways from a polycarbosilane precursor but which had different final structures, notably one was microcrystalline and the other amorphous and they contained very different amounts of free carbon. In the light of these results it seems reasonable to propose the type of structure which would be optimal for a fibre to be used in the temperature range 1000 to 1300° C.

The spread of tensile properties at room temperature appears of little significance and is due to the distribution of defects on or in the fibres. The existence of these defects is probably due to the purity and handling of the fibre during processing and not an inherent limiting factor for use at high temperature.

It is apparent that a microcrystalline structure is preferable to one which contains amorphous SiC. Above 1100° C the amorphous fibre crystallized and this was accompanied by a fall in strength. This was clearly limited by a microcrystalline structure. At the higher temperature, 1200 and 1300° C, the changes in microcrystallinity which occurred with the initially amorphous fibre allowed considerable primary creep deformation. This was much less important with the initially microscryalline fibre. The fibre structures attained equilibrium with a grain size of 3.0 nm after which they did not evolve. It seems then a fibre with an initial structure containing SiC microcrystals of 3.0 nm is preferable for use between 1200 and 1300° C. In this way the induced creep strain would be reduced to a minimum. Such a structure was obtained by heat treatment at 1300° C for between 3 and 5 h.

The free carbon content in the fibre was found to be important in blocking movement and hence creep of the structure. At 1100° C the creep threshold for the NLP 101 fibre containing 20 mol % carbon had its threshold at 0.6 GPa. However, it was also seen that the reaction SiO_2/C, which occurred at high temperature, was very damaging to the fibre. The result was that those NLP 101 fibres which could be subjected to 0.75 GPa at 1300° C resisted for more than 50 h; however, the NLM 102 fibre could not support 0.55 GPa long enough for the primary creep stage to be completed, which was 20 h. In addition, it was seen that the reaction and degradation of the fibre was greater and more rapid in argon than in air. This was presumed due to the influence of a thin layer of SiO_2 which formed on the fibre surface so limiting the diffusion of CO and SiO. It is therefore probable that the reaction rate SiO_2/C will be affected by the matrix when the fibres are used as reinforcement. The reaction rate will also depend on the porosity of the matrix.

These results indicate that the free carbon content should be controlled. The carbon content is due to the molecular structure of the precursor fibre, in particular the number of CH_3 groups, as well as the conditions of pyrolysis. Modification of these two parameters would allow changes of the free carbon content to be made.

The oxide SiO_2 exists in two forms in the fibre. It is present throughout the fibre due to the fabrication process and also as a surface layer after heat treatment. Such a surface oxide layer may have existed on the untreated fibre but was too fine to be detected. Such a thin layer could be important in protecting the fibre for short periods at high temperature. Despite this the conclusion must be that the presence of SiO_2 in the fibre is undesirable. The low viscosity of SiO_2 at temperatures between1000 and 1300° C must aid the creep deformation of the fibre. A low content of SiO_2 is therefore desirable for the finished fibre but this poses problems for its manufacture. The solution would be to cross-link the initial polymeric fibre by technique other than oxidation in air.

The conditions of load and temperature discussed in this paper are quite extreme and it is probable that the ideal fibre described above cannot be made. In addition the reactivity of SiO_2 with the free carbon can be dramatically slowed with a surface coating. The comments made here are therefore suggestions for the possible avenues of further research enabling the fibre to be improved rather than an absolute recipe.

6. Conclusions

The creep tests conducted with the two fibres revealed very different behaviours which are explained by their different microstructures.

The existence of creep stress threshold up to 1200° C for the NLP 101 fibres and to 1300° C for the NLM 102 fibres is due to the presence of carbon segregates of about 2.0 nm. The reaction of the carbon with the oxide which is present is encouraged in an argon atmosphere. In air the oxide layer formed on the fibre probably slows diffusion of the gaseous by-products. The fibre's structure changes little at 1000° C and the observed creep is probably due to the diffusion of the carbon in the body of the fibres. At 1200° C the SiC structure changes slowly towards a stable crystalline state with a grain size of 3.0 nm. This change influences considerably the creep behaviour of the NLP 101 fibre which is initially amorphous. At 1300° C the stable microcrystalline state is reached more quickly during the primary creep stage. Thereafter the secondary creep is due to diffusion and slippage of the grains. The movement in the NLP 101 structure was seen to be of a different nature in air than in argon at 1300° C. The mechanisms at 1200° C in both air and argon and in argon at 1300° C were, however, similar.

The lifetimes of the fibres in creep were seen to suffer due to the reaction between the SiO_2 and the carbon.

This study suggests that the fibre would be improved for use at high temperatures if the structure were microcrystalline with a grain size of 3.0 nm. The structure would then be stable to 1300° C. The degradation of the fibre due to the reaction C/SiO_2 would be reduced by limiting the amount of free carbon and of SiO_2 in the fibre structure.

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