Journal of the European Ceramic Society 18 (1998) 1531-1538

PII: S0955-2219(98)00069-7
0955-2219/98/$19.00 + 0.00

The Properties and Structure of the Carbon Fibre in Carbon/Carbon Produced on the Basis of Carbon Fibre Reinforced Phenolic Resin

G. Lüdenbach,[a]* P. W. M. Peters,[a]† D. Ekenhorst[b] and B. R. Müller[b]

[a]DLR, Institute of Materials Research, 51170 Köln, Germany
[b]Federal Institute for Materials Research and Testing, 12200 Berlin, Germany

(Received 22 October 1997; accepted 16 February 1998)

Abstract

The properties of carbon fibre reinforced carbon produced on the polymer route by impregnation and subsequently hardening the resin, carbonisation and graphitization depend on many variables. During processing mainly the polymer matrix (and the interface) undergoes a strong change of its structure and properties. Depending on the type of fibre used, however, also large structural fibre changes can be found. This is demonstrated in the present investigation in which two types of fibres are used: a HT-fibre (HTA of AKZO company) and a HM-fibre (M40 J of Toray Company). The HT-fibre was found to be dimensionally and structurally unstable well below the maximum fibre processing temperature of 1400°C. The fibre shrinks (the in-frozen processing stress relaxes) at temperatures as low as 850°C. The shrinkage of the fibre bundle embedded in phenolic resin during the carbonisation process is influenced by matrix shrinkage stresses and pyrolysis products. Above 1000°C the HTA carbon fibre in carbon/carbon bundles continuously changes its structure. After heat treatment at a temperature of 2800°C the structure (lattice distance, orientation of the crystallites, crystallite size) is very similar to that of HM-fibres. © 1998 Elsevier Science Limited. All rights reserved

Introduction

Carbon fibre reinforced carbon is one of the most complicated composite materials. The reason is that during processing (starting with cured carbon fibre reinforced polymer, carbonisation at 1000°C and the following graphitization at 2100°C) all its components (fibre, matrix and interface) generally change considerably. A phenolic matrix with a modulus of 3–4 GPa is transferred into a glass-carbon matrix with a modulus of 35 GPa during carbonisation.[1,2] The phenolic resin shrinks during carbonisation linearly to 80% if the process is unhindered, so that the volume is reduced to 50%.[2] The stiff carbon fibre hinders this shrinkage in the axial direction of the fibre, whereas transverse to the fibres shrinkage can take place relatively unhindered. In multidirectional carbon/carbon the shrinkage is hindered in every single fibre direction. This leads to shrinkage stresses which gives rise to a typical shrinkage crack pattern, e.g. in 2-D carbon/carbon with cracks occurring parallel to the different fibre directions (Fig. 1). Matrix cracking transverse to the fibres generally does not occur because the fibres prevent the formation and the extension of cracks in this direction due to crack bridging.

The strength of carbon/carbon after carbonisation (heat treatment temperature maximum 1000°C) generally is low (especially for low modulus carbon fibres).[3–5] The strength of carbon/carbon partly recovers (compared to the cured condition) if the material is treated at higher temperatures. This recovery is probably the result of:[3–5]

- relaxation of shrinkage stresses;
- structural change of the matrix (stress graphitization).

Further, a reduction of the fibre strength due to the formation of carbonisation products in the matrix and a subsequently recovery due to the removal of these products is under discussion.

---

*Presently at Preussen Elektra, 30457 Hannover, Germany.
†To whom correspondence should be addressed.

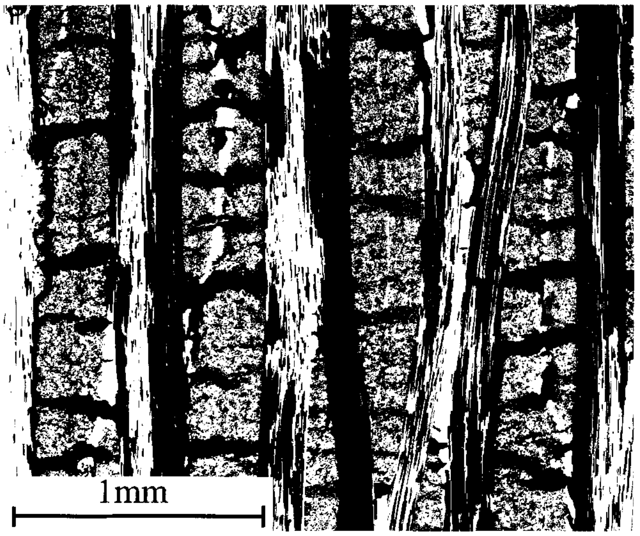

Fig. 1. Micrograph of characteristic damage state in 2-D C/C after carbonisation at 920°C.

The mechanical properties of carbon/carbon are dominated by the carbon fibre. This is also valid for the costs of these materials. For this reason in many cases carbon/carbon is produced on the basis of low cost carbon fibres, which are the HT-type of carbon fibres produced from polyacrylonitrile precursor. If these fibres are used the processing temperature during carbon/carbon production usually exceeds the maximum temperature reached during fibre production. This will lead to a structural change of the carbon fibre. In order to understand the properties of carbon/carbon it is thus necessary to deal with the properties of the carbon fibre as influenced by processing. Because of proprietary secrets the conditions under which a PAN-precursor is transformed into a carbon fibre are not exactly known. The general processing scheme, however, consists of an oxidation treatment at 250°C during which the fibres are stretched, followed by a carbonisation up to temperatures of 1500°C and a final graphitization in the temperature range of 1500–2500°C (depending on the properties required).[6]

In the first step of the process—the oxidation—the flexible polyacrylonitrile molecule is transformed in a stable oriented cyclic molecule. In the following carbonisation step gaseous waste products (mainly nitrogen and hydrogen) are removed and the structure of the fibre is transformed now in a network of extended hexagonal ribbons (a turbostratic graphite structure). The alignment of these ribbons in axial direction of the fibre is improved during the graphitization process. The orientation of the structure can further be improved by stretching the fibre at very high temperatures (2500 to 3000°C[7]). During the different processing steps the stiffness of the fibre continuously increases. The influence of processing on the strength of the fibre is, however, more complicated. The purity and processing of the precursor plays an important role. Usually a maximum strength is reached at intermediate heat treatment temperatures, which results also in a lower modulus fibre ($E = 200-250$ GPa).

The structure of the carbon fibre usually can be investigated with the aid of X-ray diffraction.[8] The most important structural parameters are the lattice spacing (d_{002}), the orientation of the crystallites (orientation parameter Z) and the crystallite size (L_c) of the basal planes, respectively. The spacing d_{hkl} between (hkl) lattice planes is given by Bragg's law:

$$\lambda = 2 \cdot d_{hkl} \cdot \sin(\Theta_{hkl}) \tag{1}$$

where λ is the used X-ray wavelength and $2\Theta_{hkl}$ is the scattering angle (2 times the Bragg angle) at which the diffraction peak is found.

In principle the crystallite dimension L_c can be determined from the analysis of the line shape of a diffraction peak through use of the Scherrer formula

$$L_c = \frac{K \cdot \lambda}{D_{00\ell} \cdot \cos(\Theta_{00\ell})} \tag{2}$$

where K is the Scherrer constant and $D_{00\ell}$ is the integral breath of the (00l)-reflexes. If we use the integral width B_h instead of $D_{00\ell}$ the Scherrer parameter K is equal to unity leading to:

$$B_h = \int_0^\infty \frac{I(b)}{I_{max}} \mathrm{d}k \tag{3}$$

where b is the distance in the reciprocal space, while $I(b)$ is the intensity distribution of the investigated Bragg reflex in the reciprocal space and I_{max} is the maximum of the distribution. Carbon fibres are also characterised by complete rotational disorder with respect to the filament axis, but partial disorder with respect to the perpendicular directions. An indicator of the preferred orientation of the basic structural units, relative to the fibre axis, is the azimuth spread of the carbon 002 reflection. The frequently used orientation parameter Z, is the full width at half the maximum intensity, obtained in the azimuth scan, measured in degrees. However a more accurate measure of the orientation of crystallites is given by

$$\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} I(\phi)\cdot\cos^2\phi\cdot\sin\phi \mathrm{d}\phi}{\int_0^{\pi/2} I(\phi)\cdot\sin\phi \mathrm{d}\phi} \qquad (4)$$

where ϕ is the azimuth angle of the d_{002} reflection arc of the carbon fibres and $I(\phi)$ is the intensity scattering at angle ϕ. The preferred orientation of crystallites in carbon fibres is strongly influenced by the processing temperature and stretching conditions. Hot stretching and heat treatment lead to a substantially increase in preferred orientation. Also the crystal dimension increases during heat treatment if the applied temperature exceeds the maximum processing temperature of the used carbon fibres. During the graphitization process usually the lattice spacing is reduced (d_{002} is approaching 0·33539 nm, which is the value for graphite crystals), the orientation improves ($\langle \cos^2 \phi \rangle$ becomes smaller) whereas generally the crystallite size increases. This structural change is accompanied by a modulus increase.

In the present investigation (which is a part of the thesis work of the first author,[4] combined with X-ray investigations performed at BAM Berlin) we concentrate on the influence of carbon/carbon processing on the dimensional and structural stability of the carbon fibre.

Materials and Experiments

Surface treated and sized carbon fibres (M40 J produced by Toray Co. and HTA produced by AKZO with properties as given in Table 1) were used as reinforcement in carbon/carbon composites (C/C). The unidirectional C/C specimens were produced by impregnation of untwisted loose bundles of 12000 carbon filaments with phenolic resin and a following carbonisation/graphitization process. The impregnation was carried out by taking off the fibre bundles from the bobbin and pulling them through a heated (60°C) impregnation bath of phenolic resin. After this they were wound around an aluminium plate and cured at 180°C in a vacuum bag at an autoclave pressure of 1 bar. The volume fraction of the carbon fibres in the C/C bundles, was about 60% for the HM- and 65% for the HT-fibre reinforced C/C bundles, respectively. Some of the cured impregnated bundles are selected for tensile testing, the others are pre-carbonised at a temperature of 500°C at DLR Köln or carbonised in an inert atmosphere for 4 h at a temperature of 920°C at Schunk Company. After carbonisation an additional heat treatment was performed at different temperatures (1000, 1400, 1800, 2100 and 2800°C for 20 h). The heat treatment procedure at 2100°C was carried out at Schunk Company, at 2800°C at the University of Karlsruhe (Inst. für chemische Technik) and at the remaining other temperatures at DLR Köln.

Table 1. Fibre properties according to the suppliers data sheets[10,11]

	Tenax HTA-12000	*M40 JB-12000-50B*
Tensile strength[a] (MPa)	3959	4520
Modulus[a] (GPa)	238·8	380
Density (g cm^{-3})	1·77	1·78
Filament diameter[b] (μm)	6·95	5·15[c]
Fibre bundle cross sectional area (mm^2)	0·455	0·250
Sizing (% of weight)	1·38	1·3

[a]Determined on impregnated and cured bundles according to DIN 65382.[12]
[b]Determined by gravimetry.
[c]Fibre cross-section kidney-shaped.

The modulus of the impregnated bundles was determined in a displacement controlled tensile test, making use of an extensometer with a gauge length of 40 mm. The contribution of the matrix to the modulus is neglected, so that the measured strain is considered to be the result of the fibres loaded to a stress determined by dividing the load by the total fibre cross-sectional area given in Table 1.

The axial thermal expansion of loose and differently treated C/C bundles was measured in vacuum with the experimental set-up given in Fig. 2. The loose and C/C bundles, with a gauge length of 100 mm between the grips, were resistance-heated with the temperature being measured with a pyrometer in the range of 500 to 2000°C. Heating and cooling was performed with a rate of 200°C min^{-1}. The axial elongation of the heated bundle was measured under a constant small weight of mainly the lower grip ($F = 1{\cdot}5\ N$) with the aid of an inductive strain gauge placed at the bottom of the vacuum chamber.

The temperature and elongation data were stored in a data recording device with a rate of 1 Hz. After application of the different heat treatments, the structure of the carbon fibre in the bundles was characterised at BAM Berlin, making use of X-ray diffraction technique. The crystalline structure was described in terms of lattice distance, orientation parameter and crystallite size. For additional information on shrinkage some dilatometer experiments (equipment Bähr 803) were performed on unidirectional and two-directional (2-D) reinforced C/Cs produced by Schunk Company. These materials carbonised for 4 h at a maximum temperature of 1100°C also contained the two types of fibres HTA and M40 J.

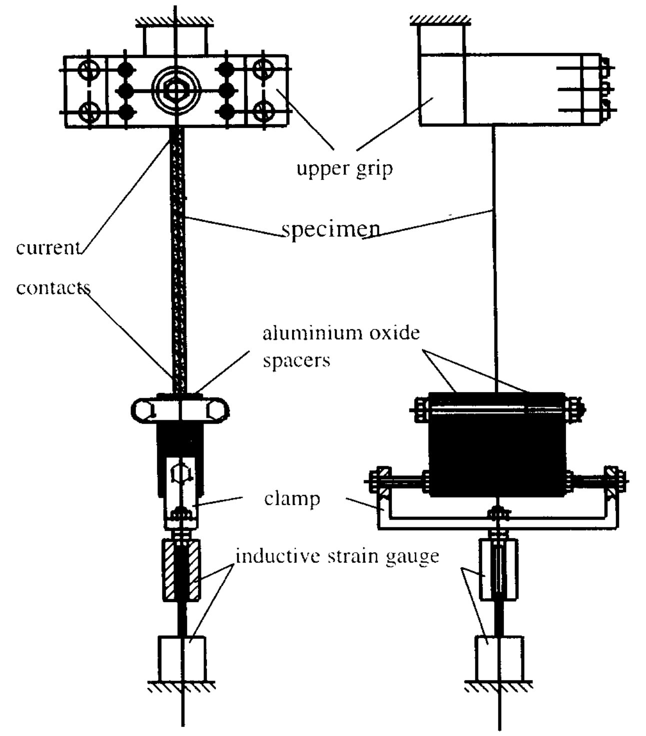

Fig. 2. Experimental set-up to measure the elongation of loose and C/C bundles due to resistance heating up to maximum temperature of 2000°C.

Results

The dimensional stability of loose HTA carbon fibre bundles was investigated by heating the bundles in a vacuum chamber as depicted in Fig. 2. Figure 3(a) shows that initially the length of the bundle increases due to thermal expansion. Above ~800°C, however, the bundle shrinks. This shrinkage process is terminated at ~1100°C and the bundle expands again at higher temperatures. On cooling down from 1600 to 500°C the slope of the length change is smaller than on heating. This is due to the structural change taking place at higher temperatures. The higher degree of graphitization of the fibre gives rise to a reduction of the coefficient of thermal expansion leading to the smaller slope on cooling down.

To study the influence of dwell times at higher temperatures a loose bundle was heated with a rate of 200°C min^{-1} up to 1000°C and this temperature was kept for 30 min. After cooling down to room temperature a second cycle was performed by heating the sample up to 1600°C. Figure 3(b) shows that the shrinkage process begins at ~830°C and is not terminated when the dwell temperature of 1000°C is reached. At 1000°C a minimum length is reached after which the fibres increase in length again but at the end of the 1000°C period shrinkage is not completely overcome. During the second cycle only a small shrinkage occurs which takes place above ~1200°C. After the two cycles the bundle has a greater length, whereas if only the dwell cycle is performed the bundle final length is smaller than the original one.

Carbon/carbon bundles with the HTA fibre type were also investigated in relation to the longitudinal elongation due to a heat treatment. The carbonisation of these bundles was performed at 920°C for 4 h at Schunk Company as mentioned before. The length change of a C/C bundle heated up to 1600°C at a rate of 200°C min^{-1} is given in Fig. 4. It demonstrates that at ~1150°C a shrinkage process begins, which is terminated at ~1450°C.

Dilatometer experiments (limited to a maximum temperature of 1350°C due to equipment requirements) on unidirectional and two-directional C/C materials with the two types of fibres (HTA and M40 J) were also performed on material carbonised at 1100°C. The results in Fig. 5 indicate that the material with HM-fibres does not show any shrinkage. The unidirectional material with HTA fibre shows a strong shrinkage, whereas the 2-D material only shows moderate shrinkage. A repetition of the thermal cycle indicates that the process of shrinkage is irreversible and practically completed after the first cycle.

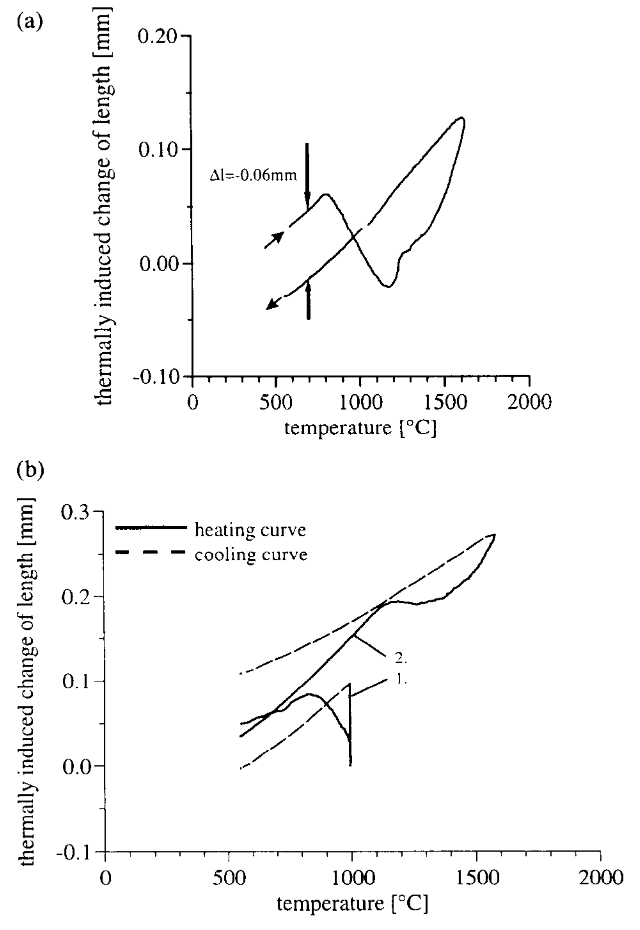

Fig. 3. Thermally induced change of the loose HTA fibre bundle length as a function of temperature: (a) from 500 to 1600°C (heating and cooling rate ±200°C min^{-1}); (b) cycle 1, heating to 1000°C with dwell for 30 min and cool down cycle 2, heating to 1600°C and cool down.

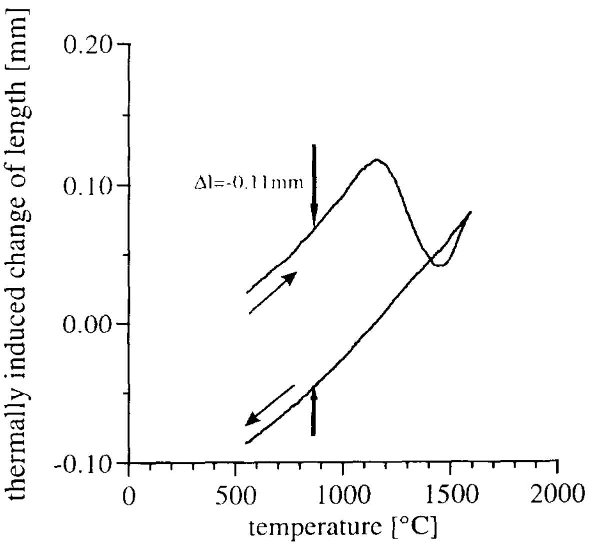

Fig. 4. Thermally induced length change of C/C bundle with HTA fibres (carbonised at 920°C for 4 h) as a function of temperature (rate ±200°C min^{-1}).

Measurements of the tensile modulus of the cured impregnated bundles and carbonised bundles treated at the different temperatures are presented in Fig. 6. The bundles with the HT-fibres clearly undergo a modulus change after heat treatments at and above 1000°C. After a heat treatment at 2800°C the modulus of the bundle closely approaches the modulus of the bundle with the HM-fibres. The heat treatment, however has practically no influence on the modulus of the bundles containing the HM-fibres except for the 2800°C treatment which increases its modulus slightly.

X-ray diffraction

To archive the structural parameters of the examined specimens, an X-ray diffraction apparatus was used according to a Guinier set up. It consists of an X-ray tube with a focusing monochromator, a diffractometer were the axis of rotation is parallel to the line of the tube focus and a counter tube with subsequent electronics and data processing. To avoid asymmetric line profiles caused by divergent X-rays a Soller slit system was used. The specimens were mounted with the orientation of the reinforcing fibres coaxial to the axis of rotation. The calibration of the angle scale (to determine the exact Bragg angle of the carbon diffraction peak) was done with the help of CaWo$_4$ powder as a reference. The measured data are analysed by a computer code taking into account the appropriate corrections and calibrations. A lorenzian profile was fitted to the intensity distribution of the diffraction peak, which delivered the lattice spacing [from the centre of the profile according to eqn (1)] and the crystallite size [according to eqns (2) and (3)]. The mean crystallite orientation distribution was estimated according to eqn (4) The results for the two types of fibres are illustrated in Fig. 7. The data of the *loose fibre bundles* are given by open circles for the HTA- and open triangles for the HM-fibres, respectively. The data for the C/C bundles are represented by the corresponding closed symbols. The first data point of each series is representing the property of the as delivered loose fibre bundle. The data agree very well with the data given in the literature.[9]

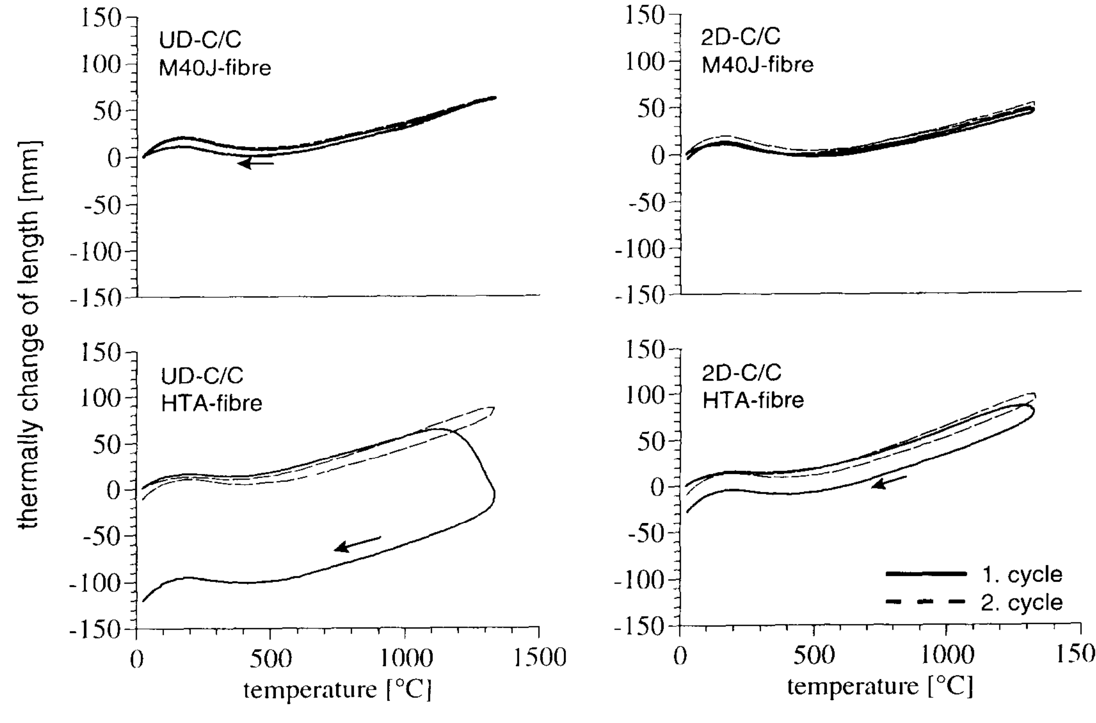

Fig. 5. Dilatometer results on length change in fibre direction for UD-C/C and 2-D-C/C material (HTA and M40-J fibre-reinforced carbon, carbonised for 4 h at 1100°C).

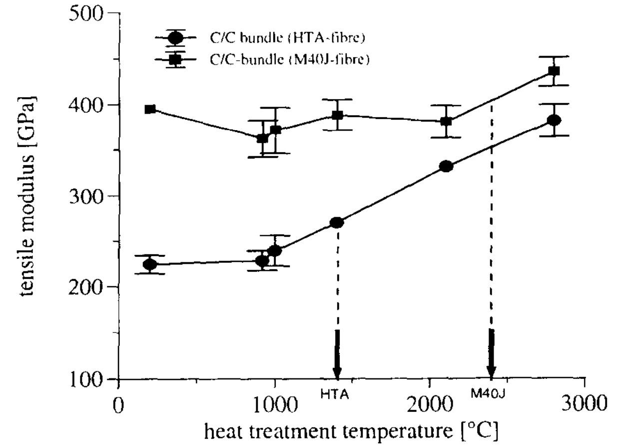

Fig. 6. Tensile modulus of the C/C bundles as a function of heat-treatment temperature.

The lattice spacing was found to be $d_{002} = (0{\cdot}3472 \pm 0{\cdot}0005)$ nm for the HTA-fibre and $d_{002} = (0{\cdot}3439 \pm 0{\cdot}0005)$ nm for the HM-fibre, respectively. For the HTA fibres an orientation of the crystallites of $\langle \cos^2 \phi \rangle = 0{\cdot}075 \pm 0{\cdot}003$ and a crystallite size of $L_c = (3{\cdot}0 \pm 0{\cdot}1)$ nm, respectively, was determined. The HM-fibres have with $L_c = (4{\cdot}5 \pm 0{\cdot}1)$ nm, a bigger crystallite size and with $\langle \cos^2 \phi \rangle = 0{\cdot}030 \pm 0{\cdot}003$ a much better orientation of the crystallites. The thermal treatment turns the HT-fibre into a HM-fibre so that after the maximum heat treatment temperature of 2100°C the structural parameters of the two types of bundles become very similar. The orientation of the crystallites increase to $\langle \cos^2 \phi \rangle = 0{\cdot}027$ for HT- and $\langle \cos^2 \phi \rangle = 0{\cdot}022$ for HM-fibres, whereas the lattice spacing reduces to $d_{002} = 0{\cdot}3421$ nm for the HT- and $d_{002} = 0{\cdot}3426$ nm for the HM-fibres, and the crystallite size increases to $L_c = 5{\cdot}9$ nm and $L_c = 6{\cdot}3$ nm, respectively. As depicted in Fig. 6, the structural change of the HT-fibre is accompanied by a strong modulus increase, whereas the significant change of the structural parameters of the HM-fibre bundles at 1800°C and higher is reflected only by a relatively small modulus increase after heat treatment at 2800°C.

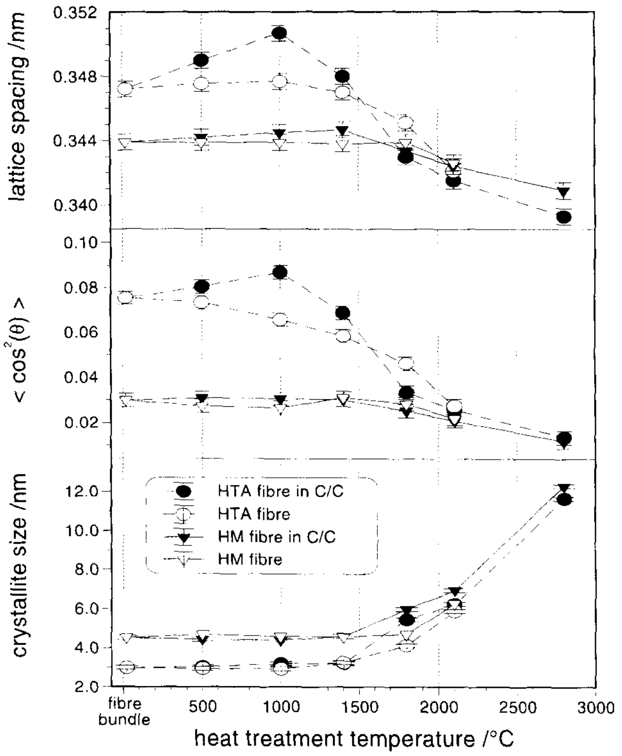

Fig. 7. Structural parameters as a function of heat treatment temperature of loose and C/C bundles with HTA and M40 J fibres. Top: lattice spacing d_{002}; middle: orientation of the crystallites; bottom: crystallite size L_c.

So far the expected behaviour of the loose fibre bundle (open symbols in Fig. 7) is observed. If we use the carbon fibres as a reinforcement in a carbon matrix produced on the polymer route, the situation changes significantly. For heat treatment temperatures up to 1000°C the lattice spacing of the used HTA fibre increases drastically up to $d_{002} = 0{\cdot}3507$ nm accompanied by a reduction of the orientation of the crystallites ($\langle \cos^2 \phi \rangle = 0{\cdot}087$) and a minor growth of the crystallite size ($L_c = 3{\cdot}2$ nm, see closed circles in Fig. 7) in comparison to the data archived for the loose fibre bundles. In principle the HM-fibres in a carbon matrix shows a similar behaviour but only to a much smaller extend (see closed triangles in Fig. 7). At the heat treatment temperatures of 1400°C the lattice spacing increases slightly to $d_{002} = 0{\cdot}3447$ nm whereas the orientation of the crystallites remains almost the same ($\langle \cos^2 \phi \rangle = 0{\cdot}030$). This behaviour is probably related to the process of shrinkage of the fibre. Its occurrence is not expected, because it has been suggested, that the structure of the carbon fibre does not change as far as the heat treatment temperature does not exceed the production temperature of the involved carbon fibre. This is not the case as can be seen in Fig. 7.

Discussion

The present investigation on carbon/carbon bundles with the HT- and HM-fibre shows that especially the HT-fibre undergoes a structural change as a function of the heat treatment temperature. Although the fibre is produced at a maximum temperature of ~1400°C it shows a structurally and dimensionally unstability even below this temperature. The occurrence of shrinkage of the loose HT-carbon fibre bundle (starting at 800–850°C) indicates, that the structural and dimensional stability is not only influenced by the applied temperature, but also by the axial stress applied to the fibre and the duration of the treatment. The HTA-fibre bundle is processed by the fibre producer at 1400°C under (an unknown) tensile stress, but in a relatively short time. Probably for this reason the in-frozen processing stress in the bundle relaxes which leads to a higher disorder or a reduced orientation. After this relaxation the graphitization process restarts also at temperatures lower than the fibre processing temperature. Investigations on carbon/carbon with two-dimensional fibre reinforcement, carbonised at 920°C, have shown,[4] that, if a sufficient high tensile load is applied onto the specimen, shrinkage can be hindered during, e.g. an additional heat treatment at 1000°C. Thus the carbon fibre bundle (either loose or in the carbon matrix) will show shrinkage due to relaxation followed by elongation as a result of further graphitization.

Now the question arises, if the shrinkage of the matrix due to the carbonisation process can enhance the shrinkage of the fibres. As mentioned in the introduction, shrinkage stresses are present in the matrix due to the transformation of the polymer matrix into the glass carbon matrix. The shrinkage of the matrix induces a compressive axial stress in the fibre. For this reason it can be expected that this axial stress causes an additional shrinkage of the fibre. This is based on the assumption that if shrinkage of the fibre can be prevented by a tensile stress, shrinkage can be increased if a compressive stress is applied. A comparison of the elongation of the loose fibre bundle [Fig. 3(b), second cycle after the simulated carbonisation cycle 1] with the elongation of the carbon/carbon bundle during a heating cycle [from 500 to 1600°C with a rate of $200°\mathrm{C\,min}^{-1}$ (Fig. 4)] shows an *elongation* of the loose bundle of 0·07 mm. On cooling down to 500°C the carbon/carbon bundle however shows a total *shrinkage* of 0·11 mm after completion of this thermal cycle. A calculation of the stress enforcing the increased shrinkage is not possible, as in contradiction to the effect of thermal expansion (without structural change) the fibre modulus during the shrinkage process is unknown. Experiments are under preparation to determine the fibre modulus during the shrinkage process.

Figure 5 shows that the shrinkage in 2-D carbon/carbon material with HTA-fibres is much less than in 1D material. The shrinkage process in the 2-D material seems to be delayed to higher temperatures.

A phenomenon not well understood in the present stage of investigation is the shift of fibre shrinkage to higher temperatures in the carbon/carbon bundles in comparison with the loose bundles. As shrinkage stresses in the matrix probably are completely established at the end of the 920°C carbonisation cycle it is not clear why the fibre at this stage has not undergone the total shrinkage process. A treatment at higher temperatures is necessary to complete the fibre shrinkage process.

In this work no attempt is made to correlate the development of the strength of unidirectional C/C with the development of the structural parameters as a function of the treatment temperature.

As mentioned in the introduction the strength of unidirectional C/C with M40 J- and HTA-fibres passes through a minimum after carbonisation at a maximum temperature of 1000°C.[4,5] It is temptative to correlate this minimum strength with the structural parameters, especially with the lattice spacing. Widening of the lattice spacing through penetration of gaseous carbonisation products in between the basal planes could introduce crystallographic stresses leading to early failure. A direct prove of this phenomenon has however not (yet) been given, so that this explanation is rather speculative.

Conclusions

Thermal treatment at temperatures below the maximum fibre processing temperature of 1400°C of loose carbon fibre HTA-bundles and these carbon fibre bundles in a carbon matrix (carbonised at temperatures up to 920°C) shows axial shrinkage of the fibre (relaxation of in-frozen axial processing stress) followed by an elongation. The investigation of the structural parameters (lattice spacing, orientation and crystallite size) has shown, that this relaxation is accompanied by an increase in disorder of the HTA-fibre, whereas the subsequently following graphitization process (producing a higher order) increases the fibre length. The M40 J fibre shows this behaviour only in tendency due to the higher fibre processing temperature of 2400°C. Axial shrinkage of the HTA-fibres and the structural disorder during the carbonisation process is influenced by induced matrix shrinkage stresses or gaseous carbonisation products. For this reason the dimensional and structural stability of the HTA carbon fibre is not only a question of temperature but also of axial stress, environment and time.

Starting at 1000°C heat treatments of carbon/carbon with HTA-fibres show a continuous change of the structural parameters (lattice distance, orientation of the crystallites with respect to the fibre axis, crystallite size) until after a heat treatment at 2800°C the structural parameters are very identical to those for carbon/carbon with the M40 J fibres.

Acknowledgement

The described research at both establishments was financially supported by the German Research Foundation (DFG), which is highly appreciated.

References

1. Glogar, P. and Balik, K., Mechanical properties and porosity of glasslike carbon. *Fortschrittsberichte der Deutschen Keramischen Gesellschaft*, 1992, **7**, Heft 3.
2. Lausevic, Z. and Marinkovic, S., Mechanical properties and chemistry of carbonization of phenol formaldehyde resin. *Carbon*, 1986, **24**(5), 575–580.
3. Zaldivar, R. J., 31 Rellic, G. S. and Yang, J. H., Fibre strength utilization in carbon/carbon. *Journal of Materials Research*, 1993, **8**(3), 501–511.
4. Lüdenbach, G., Charakterisierung des Festigkeitsverhaltens von C/C-Verbundwerkstoffen in Abhängigkeit von Behandlungs-: und Prüftemperatur. Fortschrittberichte VDI, Reihe 5 Grund- und Werkstoffe, 490, 1997.
5. Lüdenbach, G. and Peters, P. W. M., The influence of heat treatment temperature on roomtemperature and high temperature tensile strength of unidirectional carbon/carbon. In *High-Temperature Ceramic–Matrix Composites I*, ed. A. G. Evans and R. Naslain. The American Ceramic Society, Westerville, OH, 1995, pp. 285–292.
6. Chawla, K. K., *Composite Materials*. Springer–Verlag, New York, 1987.
7. Ozbek, S. and Isaac, D. Y., Carbon fibres: mechanical properties enhancement by hot stretching. In *Processing and Manufacturing of Composite Materials*. PED-Vol 49/MD-Vol 27, **307**, ASME, 1991.
8. Takaku, A. and Shioya, M., X-ray measurements and the structure of polyacrylonitrile- and pitch-based carbon fibres. *Journal of Materials Science*, 1990, **25**, 4873–4879.
9. Northolt, M. G., Veldhuizen, L. H. and Jansen, H., Tensile deformation of carbon fibres and the relationship with the modulus for shear between the basal planes. *Carbon*, 1991, **29**, 1267–1279.
10. Certification, Torayca Carbon Fiber, Toray E-TC-88-2588.
11. DIN 65382, Verstärkungsfasern für Kunststoffe, Zugversuche an imprägnierten Garnprüfkörpern, December 1988.
12. Akzo Werkszeugnis/175066, Lot-Nr. 800713.