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Mechanical properties and structure of a new commercial SiC-type fibre (Tyranno)

D. B. FISCHBACH, P. M. LEMOINE, G. V. YEN
Department of Materials Science and Engineering, University of Washington FB-10, Seattle, Washington 98195, USA

An initial evaluation of a new titanium-doped polymer-pyrolysis SiC fibre, Tyranno (Ube Industries, Ltd) showed a narrow distribution of diameters with a mean of 8.5 μm; average tensile strengths $\bar{S} \geqslant 3$ GPa, nearly independent of gauge length in the 1 to 4 cm range; Weibull parameter $m \simeq 7.3$; and mean Young's modulus $\bar{E} \simeq 170$ GPa. Heat treatment at 1300 to 1350° C in N_2 appreciably reduced S, m and E; and X-ray diffraction showed that significant crystallite growth as well as some Si_3N_4 formation had occurred. Tyranno fibre properties are compared with those of the well-known Nicalon SiC fibre.

1. Introduction

Fine, flexible fibres of silicon carbide hold considerable interest for use in metal or ceramic matrix composite materials that involve elevated-temperature processing or applications. Fibres of nominal SiC composition, made by pyrolysis of polycarbosilane polymer precursor fibres, as initially developed by Yajima *et al.* [1], have been available for several years under the trade name Nicalon from Nippon Carbon Co, Ltd. These fibres are characterized by a non-stoichiometric composition containing appreciable oxygen as well as excess carbon, and a non-crystalline or microcrystalline β-SiC type structure, and have been the subject of a number of studies (see, for example, [2–10]). They have circular cross-sections and a broad distribution of diameters in the 10 to 20 μm range, a Young's modulus E of 180 to 200 GPa and strengths of 2.5 to 3.2 GPa as received [11–13]. Despite an early report that mechanical properties of this type of fibre were unchanged at temperatures up to 1400° C [14], it is now well established [2–13] that the properties degrade appreciably with treatment at temperatures as low as 600° C, and that this degradation is fundamentally associated with the thermodynamic instability of the composition and the microstructures. Nicalon fibres are much less refractory in their behaviour than would be anticipated for SiC, and are generally disappointing with respect to high-temperature capabilities, even in non-oxidizing environments. Although some improvement in stability has been achieved by processing modifications to reduce the oxygen content (e.g. the current "ceramic grade" Nicalon), it appears that both non-stoichiometry and significant oxygen impurity levels are inherent in the nature and processing of the polycarbosilane precursor system.

Recently, a new silicon carbide-type fibre containing titanium (as well as oxygen) has been introduced by Ube Industries Ltd under the trade name Tyranno. The synthesis and pyrolysis behaviour of poly(titanocarbosilanes) have been described by Yajima *et al.* [15] and Okamura *et al.* [16], and the latter also presented information on fibres obtained from this precursor system. Evidently, the Tyranno fibres are made by a similar process [17, 18]. Tyranno fibres are claimed to have a non-crystalline structure and strength characteristics that are stable at temperatures as high as 1300° C, a significant improvement over other polymer-pyrolysis SiC fibres. Other fibre characteristics reported by the manufacturer include an unspecified composition comprising silicon, carbon, oxygen and 1.5 to 4.0 wt % Ti; circular cross-sections with a narrow diameter distribution and mean values in the 8 to 10 μm range, depending on grade; Young's modulus E exceeding 195 GPa; and strength S exceeding 2.75 GPa (gauge length not specified) with strains to failure of 1.4 to 1.7% [18, 19]. This paper reports on the results of an initial evaluation of the diameter, tensile mechanical properties and structure of a research sample of Tyranno grade TRN-M801, for ceramic applications. The mechanical properties are compared with those of Nicalon NLP-201 ("ceramic grade") measured in the same way.

2. Experimental procedure

Fibre tensile properties were measured using a modified form [20, 21] of the standard ASTM [22] single-fibre tensile test procedure. Prior to testing, yarn segments were washed with hot water or baked at 350° C in air to remove the polyethylene oxide size coating. Neither of these treatments was completely effective, but baking was better than washing. Individual fibres were carefully separated from the cleaned yarn and mounted with epoxy cement on light cardboard "picture frame" holders with gauge lengths L of 0.5, 1, 2 or 4 cm. The average diameter d of each mounted fibre was determined from laser optical diffraction measurements [21, 23, 24] near each end and at several intermediate points along L.

After alignment in the miniature pinch-type fibre grips of a table-model Instron testing machine equipped with a 500 g (maximum) load cell, the sides of the

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TABLE I Tyranno fibre diameter statistics

Fibre treatment	N	$\bar{d}_s$ (μm)	$\bar{d}$ (μm)	S.D.* (μm)	Total length (cm)
As-received	150	8.85	8.53	0.55	91
HT 1300° C, N_2	42	8.79	8.47	0.69	11

*Sample standard deviation.

mounting frame were severed with a hot-wire tool. The fibre was then successively loaded (crosshead speeds of 0.05 to 1 mm min^{-1}) and unloaded at increasing full-scale load ranges (5, 10, 20, 50 g) until failure occurred. In this way, several values of the compliance C_a (crosshead displacement per unit load, mm kg^{-1}) were obtained for each fibre, and were averaged if independent of load. The average Young's modulus $\bar{E}$ was determined from the slope of the linear plot of $\bar{C}_a$ against L/d^2 (rather than L as specified in the ASTM procedure):

$$\bar{C}_a = \left(\frac{4g}{\pi}\right)\left(\frac{1}{\bar{E}}\right)\frac{L}{d^2} + C_s \qquad (1)$$

where g is the acceleration due to gravity and C_s is the system compliance resulting from deflection of the load cell, grips, mounting tabs and glue joint*. This method of plotting largely removes the scatter that would otherwise result from a distribution of fibre diameters. Strength was computed from the failure load and the fibre diameter d. No fractography was attempted because the fibres generally shattered on failure.

The fibre microstructures was investigated by scanning electron microscopy (SEM) using a Cambridge Stereoscan with energy-dispersive X-ray analysis (EDAX) and by X-ray diffraction (XRD) using a Norelco diffractometer with graphite monochromator and Cu$K\alpha$ radiation. The XRD patterns were obtained from segments of yarn arranged lengthwise in a standard powder sample holder.

Fibres were examined in both the as-received (AR) condition and after heat treatments (HT) in flowing N_2 at 1300° C for 12 h (350° C size removal), and at 1350° C for 24 h (size removed with hot water). These heat treatments were done in a small graphite-tube resistance furnace with the yarn segments contained in a graphite boat.

3. Results and discussion

3.1. Fibre diameter

SEM observations confirmed that the Tyranno fibres have circular cross-sections. The distributions of the "raw" diameters d_s, computed using the Fraunhofer slit approximation to the diffraction equation [23], are shown in Fig. 1 at increments of $\frac{1}{3}$ μm. Results were obtained for AR and 1300° C HT fibres. In both cases, the distributions are narrow but somewhat asymmetrical, with a tail extending on the high side. Actual diameters d are smaller by 3 to 4% as a result of correction for the small, diameter-dependent difference between the slit approximation and the proper

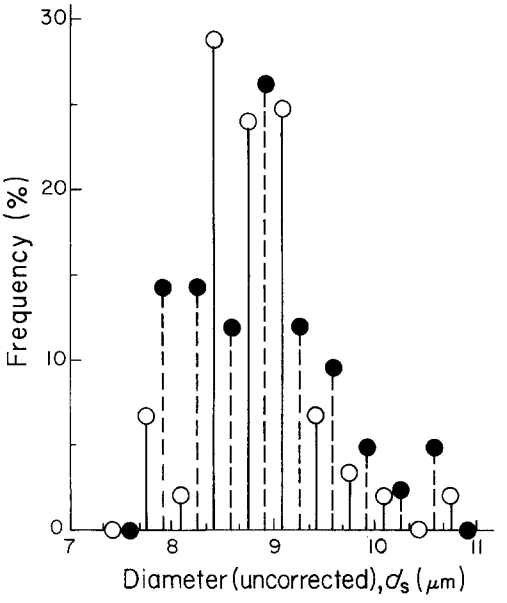

Figure 1 Distributions of Tyranno fibre diameters, measured by optical diffraction (slit approximation), (○) as-received (AR) and (●) after 1300° C heat treatment (HT).

diffraction equation for thin rods [21, 23]. The results of statistical analyses of these distributions are given in Table I.

Heat treatment had little effect on $\bar{d}_s$, but broadened the distribution somewhat. Most of the diameter variation occurred from fibre to fibre. Variation along the length of individual fibres was small. Only two of 35 AR fibres and one of 15 HT fibres had fluctuations about their means exceeding 2% (the maximum observed was +6%, −8% for a 4 cm AR fibre with $\bar{d}_s$ = 8.8 μm). The corrected mean diameters of the individual fibres, which were used to compute the mechanical properties, had distribution characteristics similar to those of the corresponding d_s data sets.

3.2. Tensile compliances and Young's modulus

After an initial decrease at low loads ($\leqslant$ 2 g), attributed to fibre straightening, the observed compliances C_a were independent of load, all the way to failure. From this it can be inferred that Young's modulus E is independent of tensile strain. There is very little scatter in the plots of $\bar{C}_a$ against L/d^2 (Fig. 2). For the AR fibres, data were obtained at L = 1, 2 and 4 cm. The HT fibres were weaker and tended to stick together (perhaps due, in part, to incomplete size removal prior to treatment), and it was difficult to separate long fibres from the yarn. Data were obtained only for L = 0.5 and 1 cm for the 1300° C HT fibres. After the 1350° C HT it was not possible to extract and mount even these short fibres. The lines in Fig. 2 represent linear regression fits to the data. The behaviour of Nicalon fibres [13], AR (L = 0.5, 1, 1.5, 2, 3, 4 and 5 cm) and 1350° C HT (L = 1, 2, 4 cm) is also shown for comparison (abscissa values are smaller because d is larger). The compliance analysis results are summarized in Table II.

*It has been found that C_s, the L = 0 intercept of the plot of Equation 1, is not a true "machine constant", but depends on fibre type and treatment. However, it is not generally necessary to evaluate C_s since $\bar{E}$ can be determined directly from the slope.

TABLE II Compliance analysis and Young's modulus

Fibre treatment	N	C_s (mm kg^{-1})	$\bar{E}$ (GPa)	Correlation coefficient
Tyranno				
As-received	35	1.71	171	0.999
HT 1300° C, N_2	12	0.53	140	0.997
Nicalon				
As-received	40	1.26	193	0.994
HT 1350° C, N_2	14	0.93	206	0.995

The mean modulus $\bar{E}$ = 171 GPa of the AR Tyranno fibres is significantly lower than the $\geqslant$ 196 GPa value specified by the producer. After 1300° C HT, $\bar{E}$ is further reduced by ~ 18%. For AR Nicalon, $\bar{E}$ = 193 GPa, and the modulus increased by about 7% with 1350° C HT. The low modulus value obtained for AR Tyranno cannot be attributed to systematic measurement error. Moduli of 14 individual L = 4 cm fibres, computed from their corrected compliances, $(\bar{C}_a - C_s)$, ranged from 165 to 176 GPa with a mean of 171 GPa and a standard deviation of 3.3 GPa. The mean moduli of three different grades of AR Nicalon (NLM-102 and NLP-101 as well as NLP-201), measured by the same technique used for Tyranno, were 192 to 196 GPa [13].

3.3. Strength

Although the elastic modulus of Tyranno was lower than expected, the strengths of the AR fibres were high and nearly independent of gauge length, as shown in Fig. 3. After 1300° C HT, the strength at L = 1 cm was reduced by nearly a factor of 1/5 and the gauge length dependence was increased. The lines in Fig. 3 represent linear regression fits to the equation

$$\log \bar{S}(L) = \log \bar{S}(1) - n \log L \qquad (2)$$

where $\bar{S}(L)$ and $\bar{S}(1)$ are the mean strengths for gauge lengths L and 1 cm, respectively, and $0 \leqslant n \leqslant 1$. $\bar{S}(1)$ is a characteristic strength dependent on critical flaw severity, whereas n, a measure of the gauge length dependence, depends on the flaw distribution. The strength behaviour of Nicalon [13], AR and after 1350° C HT, is also shown in Fig. 3 for comparison. Although Nicalon has lower strength and greater gauge length dependence than Tyranno in the as-received condition, after heat treatment the strength of Nicalon is higher than that of Tyranno for all L. These strength results are summarized in Table III. Tyranno strains to failure, computed from $\bar{E}$ and individual strength values, ranged from 1.2 to 2.6% AR, and 0.2 to 0.9% after 1300° C HT. Failure strains of Nicalon are somewhat smaller (0.5 to 2.3% AR, and 0.3 to 0.6% after 1350° C HT), due in part to the higher modulus.

On the basis of these initial results, the elevated-temperature stability of the mechanical properties of Tyranno is disappointing, and indeed inferior to that of Nicalon. However, this question deserves further investigation. In this regard, it is noteworthy that (a) the treatment temperatures used here equal or exceed the maximum stability range (1300° C) claimed by the producer; and (b) size-coating residues on the fibre surfaces could have contributed to the observed strength degradation; however, (c) Okamura *et al.* [16] observed a rapid drop in the strengths of their SiC–TiC fibres with treatment at temperatures above 1200° C (in flowing argon).

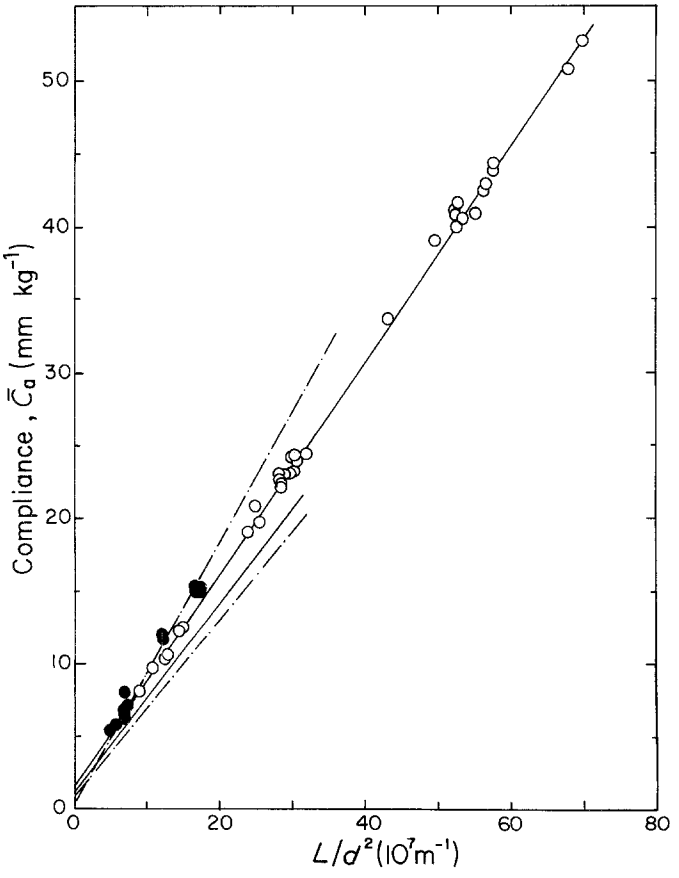

Figure 2 Mean compliances $\bar{C}_a$ of (–○–) AR and (·–●–·) HT 1300° C Tyranno fibres, plotted according to Equation 1. L = gauge length, d = fibre diameter; lines are linear regression fits. Behaviour of Nicalon fibres is also shown: (——) AR, (–·–) HT 1350° C.

TABLE III Strengths of Tyranno and Nicalon fibres

Fibre treatment	L (cm)	N	$\bar{S}$ (GPa)	S.D. (GPa)	$\bar{S}(1)$ (GPa) (Equation 2)	n
Tyranno						
As-received	1	7	3.28	0.81		
	2	14	3.07	0.48	3.25	0.06
	4	14	3.03	0.40		
HT 1300° C	0.5	7	0.80	0.34	0.69	0.22
	1	6	0.69	0.22		
Nicalon						
As-received	0.5 to 5	42 (total)			2.47	0.18
HT 1350° C	1, 2, 4	13 (total)			0.89	0.12

3.4. Weibull analysis of Tyranno strengths

The linearized form of the two-parameter Weibull distribution of the strengths S of uniform-diameter fibres of length L is [25]

$$\ln \ln [1/(1 - F)] = m (\ln S - \ln S_0) + \ln L \quad (3)$$

where the cumulative probability of failure $F = R/(N + 1)$ is determined by ranking (R) the N strengths according to increasing values; the location parameter S_0 is related to $\bar{S}(1)$; and, ideally, the dispersion parameter $m = 1/n$. Both the weak gauge-length dependence and the relatively modest scatter of the strengths (Table III) suggest that m is fairly large for AR Tyranno. There are insufficient data for meaningful Weibull analysis at $L = 1$, and N is marginal for $L = 2$ and 4 cm; but rough analyses gave approximate m values ranging from 4.5 to 8. To obtain a better estimate, the strengths measured for $L \neq 1$ were normalized to equivalent $L = 1$ cm values by multiplication by $L^{1/m}$, then merged with the measured $L = 1$ data to form a single set of $N = 35$ values [26]. Initially, an estimated value of $m \sim 6$ was used for the normalization. Analysis of these normalized data using Equation 3 with $L = 1$ gave $m \sim 7.5$, and the original data were then re-normalized using this value. A similar procedure was used to analyse the strengths of the heat-treated fibres (normalization initially with $m \sim 3$ and finally with $m \sim 4.2$). The results are shown in Fig. 4 where the lines are linear regression fits. (The lowest five AR and lowest three HT values were excluded in computing the fits.) The resulting parameters are summarized in Table IV.

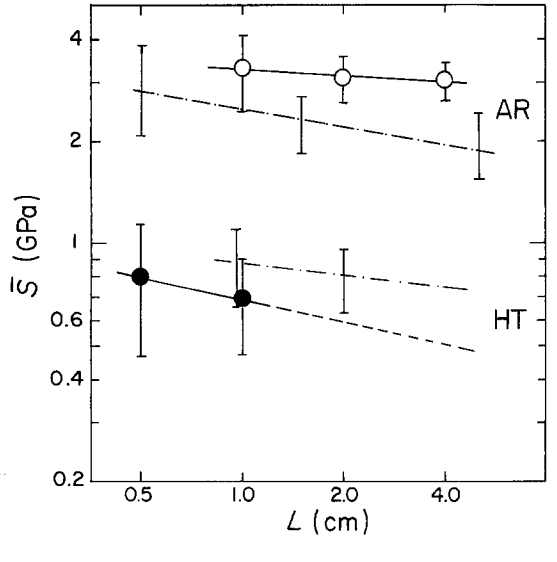

Figure 3 Log–log plot of mean strengths $\bar{S}$ against gauge length L for Tyranno fibres, (–○–) AR and (–●–) 1300° C HT. Bars show standard deviation; lines are linear regression fits (Equation 2). Behaviour of Nicalon is also shown: (–·–) AR and 1350° C HT.

From Fig. 4, the distribution for the AR fibres appears to be unimodal, but the plot for the heat-treated fibres suggests a bimodal distribution [27]. Heat treatment reduced the apparent m value by about 40% and the S_0 value by 80%. The Weibull mean strength values, $\bar{S}(L)_W = S_0\Gamma[1 + (1/m)]L^{-1/m}$ [25], computed using the parameters obtained from the normalized data, agree reasonably well with the measured mean values, but $1/m$ is larger than the observed n, as also reported for Nicalon [2]*. For comparison, preliminary analysis of normalized strength data for AR Nicalon (NLP-201) gave $m \sim 3.5$; and m values of 3.8 to 5.3 [2], 2.2 to 2.7 [4] and 4.7 [27] have been reported for other Nicalon grades in the $0.5 \leqslant L \leqslant 5$ cm range.

3.5. Scanning electron microscopy and X-ray diffraction

SEM examination of the Tyranno fibres showed that the external surfaces were smooth and featureless, and the fracture surfaces were glass-like. There were no striking differences in the appearances of the AR and 1350° C HT fibres. A trace of titanium (as well as a very strong silicon signal) was observed by EDAX of the fracture surface of an AR fibre.

X-ray diffraction observations provide some further insight into the structure of Tyranno and the effects of heat treatment on it. Smoothed tracings of typical XRD patterns for AR and HT fibres are shown in Fig. 5. With the exception of the very weak feature at $2\theta \sim 22.5°$, the broad pattern of the AR fibres resembles that obtained from Nicalon (microcrystalline

TABLE IV Weibull analysis parameters for Tyranno strengths (data normalized to $L = 1$ cm)

Fibre treatment	N	m	S_0 (GPa)	Correlation coefficient, (N')*	$\bar{S}(1)_W$ (GPa)
As-received	35	7.3	3.72	0.992(30)	3.49
HT 1300° C	13	4.1	0.77	0.996(10)	0.70

*N' = number of data used for linear regression fit.

*Values of the gamma function $\Gamma[1 + (1/m)]$, which range from 0.886 ($m = 2.2$) to 1.0 ($m = \infty$), may be found in mathematical tables.

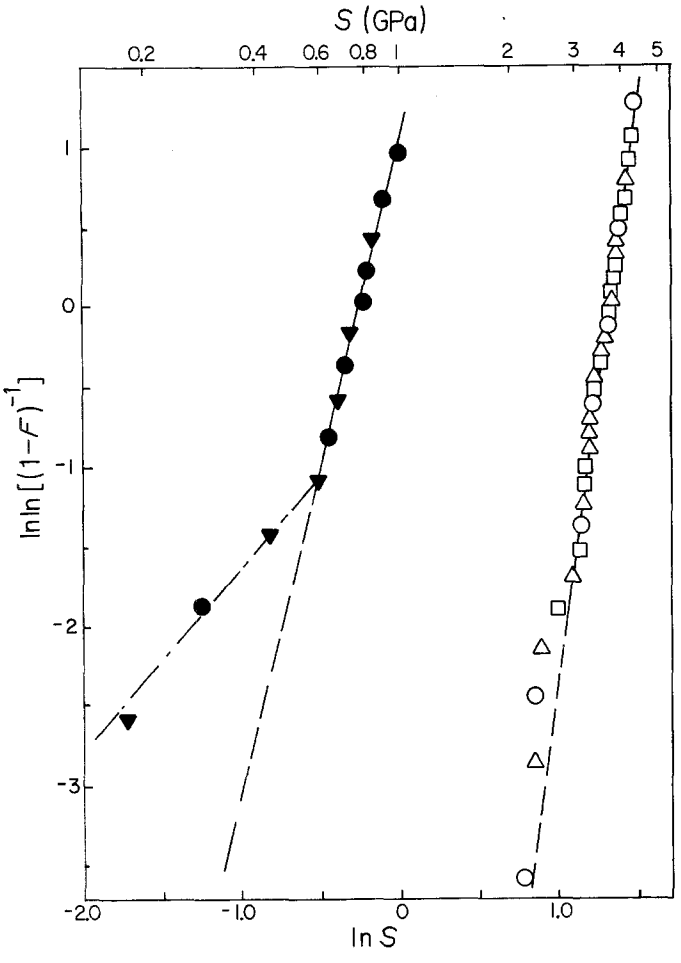

Figure 4 Linearized Weibull plots of Tyranno strength data, normalized to L = 1 cm. Lines are linear regression fits (omitting lowest data points). Open symbols, AR (m = 7.3); filled symbols HT 1300° C (m = 4.1). L = (▼) 0.5 cm; (○, ●) 1.0 cm; (△) 2.0 cm; (□) 4.0 cm.

β-SiC). However, it appears that the strongest Tyranno line, at $2\theta \sim 35°$, may actually be a super-position of two adjacent lines, and there is consistent indication of weak shoulders or peaks in the 38 to 40° and 75° to 76° ranges. Heat treatment produced a number of changes in the pattern: significant narrowing of the major lines at 2θ, ~36, ~61 and ~72° indicative of crystallite growth; noticeable asymmetry of the lines at ~61 and ~72°; the appearance of a weak and relatively narrow line at $2\theta \sim 42°$ that is not generally detectable in Nicalon; a very weak but fairly sharp line at 26.5°; and very weak trace indications of silicon nitride.

These Tyranno XRD patterns are similar in many respects to the results reported by Okamura *et al.* [16] for pyrolysed and heat-treated poly (titanocarbosilanes) with Ti/Si atomic ratios of 0.05, 0.10 and 0.15, and for fibres prepared from these precursors, though there are a number of differences in the detailed characteristics. As noted by those authors, the major features can be interpreted in terms of a superposition of the similar but not identical diffraction patterns of β-SiC and TiC. However, the apparent TiC intensities are surprisingly high in view of the low titanium content of Tyranno, reportedly only a few weight per cent [17, 18]. The positions and relative intensities of the crystalline powder diffraction lines of these two materials and of α-Si_3N_4 [28] are also shown in Fig. 5. The line at 2θ, ~42° which does not appear for Nicalon, may be attributed primarily to the (2 0 0) of TiC, the strongest reflection for that material. The remaining strong lines, at $2\theta \sim 36$, 61 and 72°, are assignable to β-SiC–TiC composite (1 1 1), (2 2 0) and (3 1 1) reflections, respectively; and a very weak peak at 2θ, ~76° corresponding to the composite (2 2 2), was often detectable as well. The line at $2\theta \sim 26.5°$ in the HT patterns corresponds approximately to the medium-intensity (2 0 0) of α-Si_3N_4. However, it also appears (unidentified) in the Okamura *et al.* patterns for the pyrolysed precursors and very weakly in some of their patterns for fibres (which were air-cured at room temperature and HT in argon). All of their fibre patterns also had a strong broad line at $2\theta \sim 22°$, attributed to cristobalite, which appears only very weakly in the Tyranno patterns.

The uncorrected breadth of the strong (1 1 1) line corresponds to an apparent crystallite size of ~1 nm in the AR Tyranno, while the (1 1 1), (2 2 0) and (3 1 1) lines of the HT fibres give sizes of ~2 to 2.3 nm after 1300° C and ~2.3 to 2.5 nm after 1350° C. These values are certain to be too small because of the composite nature of these lines, as well as the possible contribution of lattice distortion and the fact that no correction was made for instrumental broadening. However, the indication that the mean crystallite size was at least doubled by the heat treatments should be valid. Crystallite sizes reported for Nicalon [2 to 4, 6, 8, 10] range from 1 to 4 nm AR and from 2 to 10 nm after HT in H_2, argon or N_2 at $1200 \leqslant T \leqslant 1400°$ C. The uncorrected breadth of the (2 0 0) line in the HT Tyranno patterns, which is apparently due predominantly to TiC, gives a crystallite size of ~9 nm. The small but narrow spike at $2\theta \sim 35.6°$ on top of the composite (1 1 1), which corresponds to crystals larger

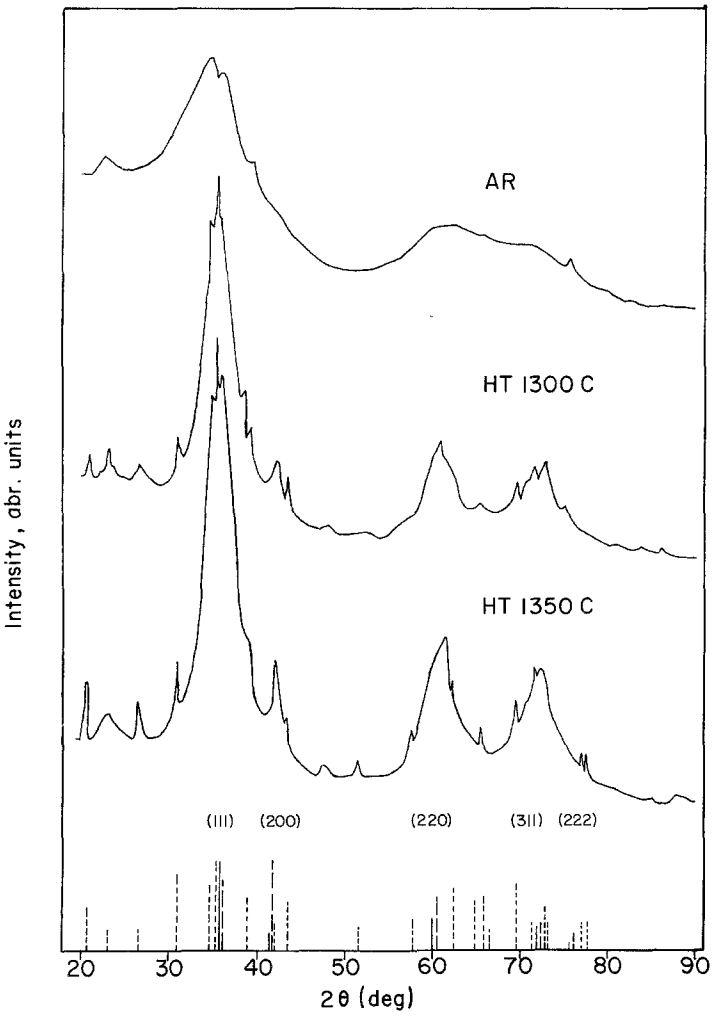

Figure 5 X-ray diffraction patterns (Cu$K\alpha$) of Tyranno fibres. All patterns are at the same intensity scale, but zero-shifted for clarity. Powder diffraction data for crystalline (——) β-SiC, (— —) TiC and (– – –) α-Si_3N_4 are also shown [28].

than 40 nm, may result from either α-Si_3N_4 or β-SiC. It is clear then that the heat treatments at 1300 and 1350° C resulted in significant crystal growth as well as some reaction forming silicon nitride, both of which may contribute importantly to the severe loss of strength that was observed.

4. Conclusions

A preliminary evaluation was made of Tyranno, a new titanium-doped polymer-pyrolysis SiC fibre produced by Ube Industries. The producer's information regarding circular cross-section; small, uniform diameters; and high tensile strengths were confirmed. In addition, it was found that the strength is insensitive to gauge length over the range 1 to 4 cm, with an approximate Weibull modulus $m \simeq 7.3$. For the lot and grade tested, Young's modulus E was found to be $\sim 13\%$ smaller than the minimum value specified by the producer. Heat treatment in N_2 at 1300 and 1350° C caused significant crystal growth and some reaction to form silicon nitride, and resulted in appreciable decreases in E and m and severe strength degradations. Further investigation at lower temperatures is required to test the producer's claim of structural and strength stability below 1300° C.

Acknowledgements

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