Improved Mechanical Properties of SiC Fibers Pyrolyzed from Polycarbosilane under Tension

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ABSTRACT

Factors that influence the mechanical properties of polymer-derived SiC fibers vary from the polymer structure to firing conditions, among which firing tension was studied in this paper. Tensile strength, Young's modulus, density, shrinkage and diameter were recorded as characteristics of SiC fibers obtained under different tensions and a great improvement of tensile strength, from 1.70GPa to 1.90GPa, could be achieved by using an optimal two-step tension schedule. From the SEM and XRD analysis, we believe that firing tension has two ways to improve the mechanical properties of SiC fibers; one is to eliminate bend portions and the other, to slightly induce the crystallization.

Key Words: silicon carbide fiber, mechanical property, tension, polycarbosilane, pyrolysis

I. INTRODUCTION

The development of Nicalon fibers, obtained by pyrolysis from organic or organometallic polymeric precursors, is exciting considerable interest as it offers the possibility of developing a new generation of composites for high temperatures. The pyrolysis processing route has some important advantages with respect to more conventional techniques /1,2/: (1) it requires lower temperatures, (2) polymeric precursors can be obtained under different states before firing (e.g. as bulk bodies, green films or fibers), (3) polymeric precursors are available with a variety of compositions as single species or as mixtures, a feature allowing the design of ceramics with specific properties.

However, the pyrolysis processing also has some fundamental disadvantages. Weight loss caused by the evolution of small species such as hydrogen and methane is fatal to the mechanical properties of SiC fibers, because many defects are formed during the pyrolysis process. For example, during the pyrolysis, considerable volume shrinkage occurs accompanied by considerable weight loss and density increase /2/, and at the same time, a compressive stress arises. To balance this stress, as expected, too low a tensile stress cannot take effect and a too high one may result in the cracking of filaments or the whole bundle.

Although commercial SiC-based fibers have been produced from various polycarbosilanes, not much literature has been published on the pyrolysis under tension. Yajima pointed out the importance of firing tension in the preparation of high strength SiC fibers as it can eliminate bend portions /3/; unfortunately, however, no tensile schedule was suggested in the patent.

To prepare high strength and high modulus carbon fibers, one often thinks of a considerable stress on the cured polyacrylonitrile (PAN) fibers before and/or

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during pyrolysis /4/. However, this technique cannot be directly adopted for the cured polycarbosilane fibers because their strength is still much lower before pyrolysis or even at lower pyrolysis temperatures. And the question arises as to which specific tension schedule is the most suitable for the pyrolysis of cured polycarbosilane fibers, since their strength increases remarkably with increase of pyrolysis temperatures and could be as high as that of carbon fibers after pyrolysis/2/.

Therefore, in this paper we are going to discuss, from an experimental point of view, how the firing tension takes effect and which specific tension schedule is more practical for the pyrolysis of polycarbosilane bundles as far as the mechanical properties are concerned.

II. EXPERIMENTAL PROCEDURE

Polycarbosilane (PCS), as the precursor of SiC fibers, was synthesized from polydimethylsilane (PDMS) at ambient pressure without using an autoclave /5,6/. It was spun into yarns through a multiorifice plate /7,8/ and heated in air up to 200°C with a weight gain of 12-14wt%. This kind of air-cured PCS yarn, as characterized in Table 1, was used as the starting material in this study.

During the study, a set up like Fig. 1 was adopted. SiC yarn or its precursor PCS yarn was set to the hot zone (about 40cm long, up to 1250°C), with tension loaded on the two ends through carbon yarns. High purity nitrogen gas, 99.999%, was flowing through the quartz tube as a protection atmosphere. Tension was loaded by adjusting the load cell. A ruler was used to record the axial length of SiC fibers and the heating rate was fixed as 100°C /h.

Fig.2 is the schematic diagram for the fixed-shrinkage test, which was placed at the hot zone in the above furnace when needed.

III. CHARACTERIZATIONS

The monofilaments were tensile tested at room temperature with a single yarn strength tester (YG-002, China). For each value, a batch of more than 25 monofilaments were tested with a gauge length of L=25mm and the data were used to determine the mean ultimate tensile strength, σ^R, and Young's modulus, E.

Table 1

Characteristics of the as-received air-cured PCS yarn

Weight gain (wt%)	Reaction degree of Si-H bond[*](%)	Gel content (%)	Number of filaments	Diameter (μm)
12-14	85-90	100	100	20-22

[*]Derived from IR spectra.

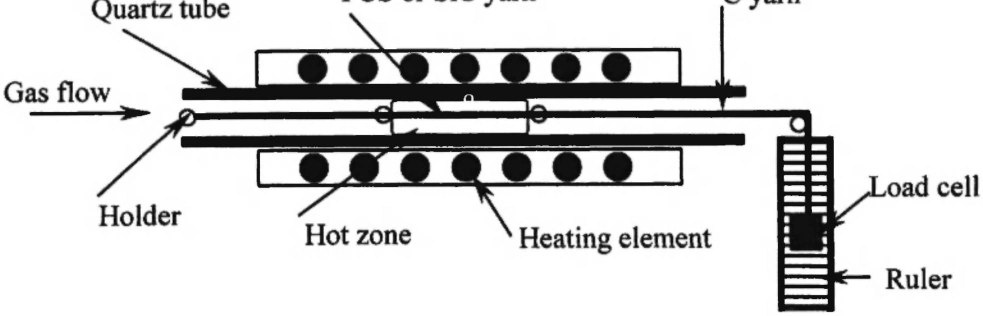

Fig. 1: A furnace with a load cell used in the study

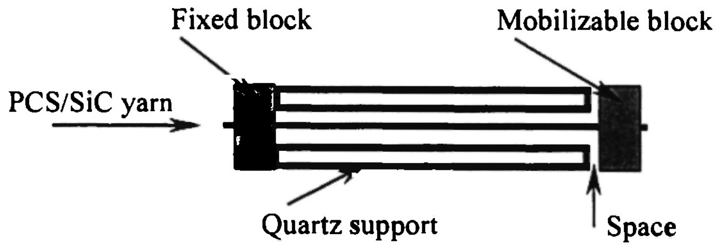

Fig.2: Schematic diagram for the controlled-shrinkage experiment

Diameter was tested using the micrometer caliper., and density was performed by the sink-float method according to a simplified ASTM C729-75 standard test. Solutions with densities of 2.30 to 3.20g/cm^3 were prepared by mixing bromonaphthalene and sym-tetrabromoethane at room temperature with increments of 0.05g/cm^3.

The X-ray diffraction (XRD) spectra (Cu-K_α/Seimens D-500 diffractometer, Germany) were recorded for the SiC fibers. The apparent mean grain size (L) of the β-SiC crystalline phase present in the samples was calculated from the width (D) of the (1 1 1) diffraction peak at mid-height, according to the following Eq. 1:

$$L = K\lambda / D\cos\theta \qquad (1)$$

where K is a constant (taken as 1), λ, the Cu-K_α wavelength (i.e. λ=0.154nm), and θ, the Bragg angle (θ=17.8°forβ-SiC(1 1 1)).

The morphology changes of the fibers after pyrolysis were studied by scanning electron microscopy (SEM) (X-650, Japan). Samples were sputter coated with a layer of Au to enhance their conductivity before observation.

IV. RESULTS AND DISCUSSION

4.1 Variations of mechanical properties as a function of pyrolysis temperature

Pyrolysis is a conversion process from organic polymer to inorganic ceramic materials /9,10/. Therefore, density changes remarkably from 1.1-1.2g/cm^{-3} to 2.4-2.5g/cm^{-3}. So does diameter (from 22 μm to 14 μm), tensile strength (from 100-200MPa to 2000MPa), and Young's modulus (from 5-15GPa to 200GPa). Their typical behaviors are illustrated in Fig. 3.

As shown in Fig. 3, great changes occur from 600°C to 800°C because the main conversion process is just in this range, during which a weight loss up to ~10wt% could be recorded /2,9,10/. The weight loss is due to the evolution of gaseous species mainly in the form of methane and hydrogen as a result of broken lateral chains and chain ends. As hydrogen evolves from the precursor system, structure changes from the organic nature to an amorphous mineral state. SiC-based fibers obtained in this way could be described as a continuum made of SiC_4 and $SiC_{4-x}O_x$ tetrahedral species containing clusters of carbon atoms /2/. The size of the domain of homogeneity varies from fiber grade to fiber grade and is of the order of 1nm.

It is well accepted that the mechanical properties of the precursor fiber are closely related to the structural evolution state. Take tensile strength, for example: the air-cured precursor fiber is as weak as 100-200MPa but it could become as strong as 2000MPa as a ceramic fiber, an increase of about 10 times. Therefore, using a uniform tension to prepare SiC fibers is not practical. As will be discussed below, considerable volume shrinkage (e.g., axial shrinkage) could also be observed as a result of the structure evolution and weight loss. Then one may be ready to think of loading tensions by limiting the shrinkage to a certain range.

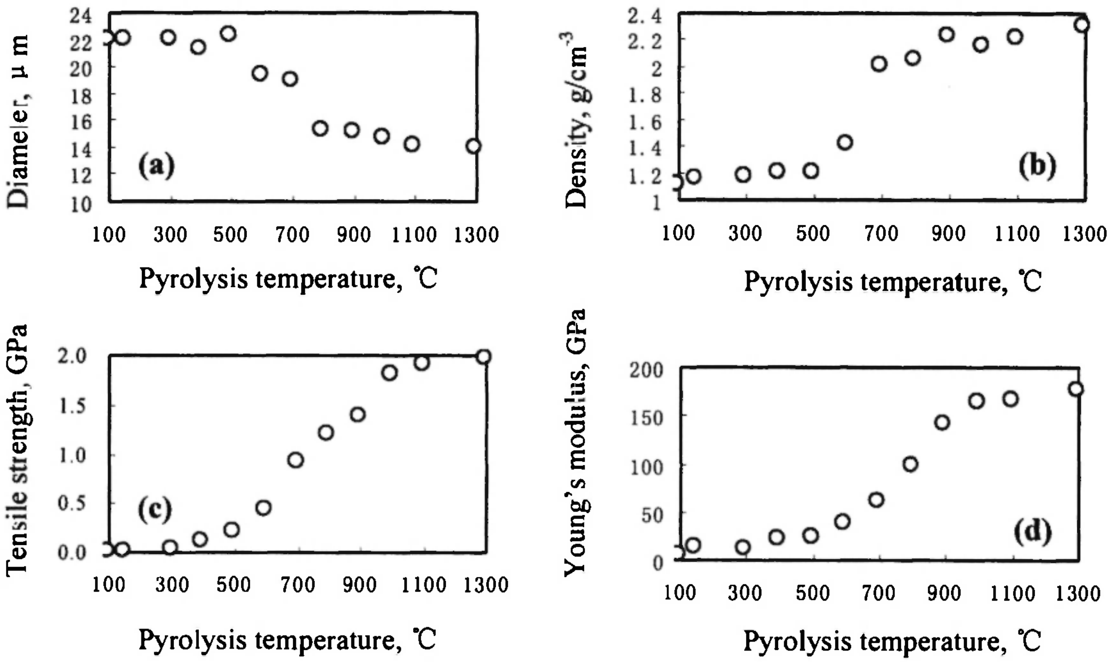

Fig.3: Variations of (a) diameter, (b) density, (c) tensile strength and (d) Young's modulus as a function of pyrolysis temperature

4.2 Effect of controlled-shrinkage on the mechanical properties of SiC fibers

To carry out the controlled-shrinkage experiment, the maximum shrinkage should first be known. Thereby, the variations of axial length and axial shrinkage of PCS yarn as a function of pyrolysis temperature were performed and illustrated in Fig. 3.

As shown, when tension is loaded (even if it is light), there is a slight tension-induced elongation beginning at 200°C and over at 540°C. Shrinkage occurs at 540°C. In general, the shrinkage can be divided into four stages, that is, an expansion stage (200°C-540°C), a fast-shrinking stage (540°C-800°C, -8% per 100K), a slow-shrinking stage (800°C-1000°C, -2% per 100K) and a near plane stage (1000°C-1200°C). During the first stage, not shrinking but expansion occurs because the material is still in an organic state and its expanding extent is somewhat related to its structure and the load weight; a large shrinkage occurs at the second range, which corresponds to the organic to inorganic transition process associated with large changes of other chemical and physical properties /2,9,10/; the fibers shrink slowly at 800°C to 1000°C, during which a slow weight loss could be observed in TGA due to the evolution of residue hydrogens /2/; after 1000°C, the axial shrinkage changes little at the final range. In short, the elongation is related to the softening and expanding of the organic precursor and the shrinkage, as mentioned above, is a result of the weight loss and structural evolution.

Two lines are shown for comparison in Fig. 4, which correspond to the heating rates of 100°C/h and 400°C/h, respectively. The maximum shrinkage differs greatly at different heating rates, i.e., the higher the heating rate the higher is the shrinkage. Specifically, a heating rate of 400°C/h means a maximum shrinkage of 30-35% and a heating rate of 100°C/h gives 25-27%. This is usually because the higher the heating rate the more is the weight loss /9/. In addition, the higher the heating rate the lower is the tensile strength, therefore, to be good for the mechanical properties, 100°C/h was adopted for all the following experiments. Table 2 shows the results of the controlled-shrinkage experiment.

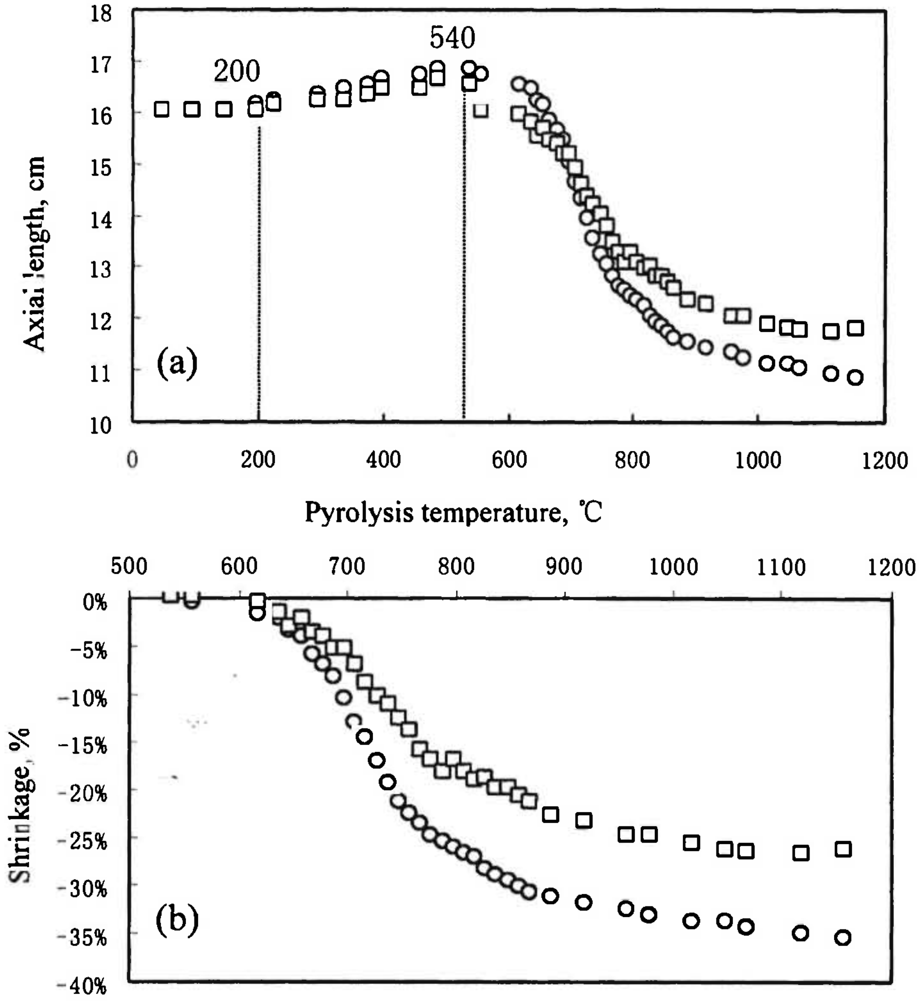

Fig.4: Variations of (a) axial length and (b) shrinkage of PCS or SiC yarn as a function of pyrolysis temperature under slight tension (1cN/yarn), in which □-line represents a low heating-rate (100°C/h) and -line, a high heating-rate (400°C /h)

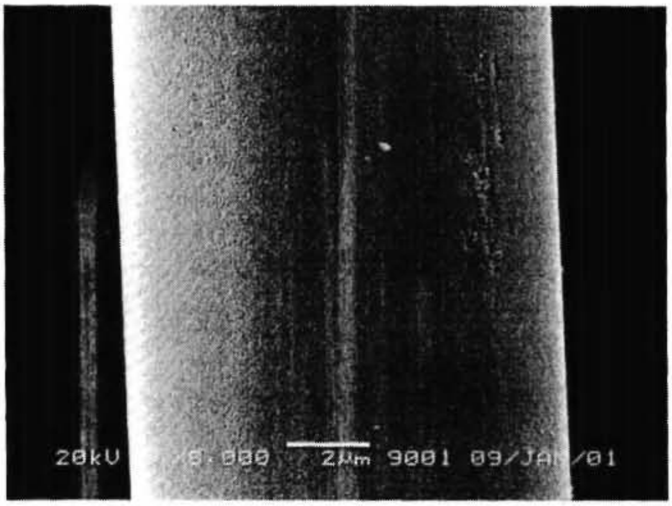

Fig.5: Axial cracks formed on the surface of a SiC filament

Table 2

Mechanical properties of SiC fibers obtained with controlled-shrinkages

Shrinkage, %	Tensile strength, GPa	Young's modulus, GPa	Remarks
0	0.74	158	Broken, straight
5	0.99	164	Broken, straight
10	1.23	161	Partially broken, straight
13	1.33	160	Partially broken, straight
16	1.60	160	Partially broken, straight
20	1.88	160	Partially broken, straight
23	1.92	165	No broken, straight
26	1.80	158	No broken, straight
30*	1.70	141	No broken, entangled

*Which means almost no tension added, for the PCS's average-shrinkage is ~26%.

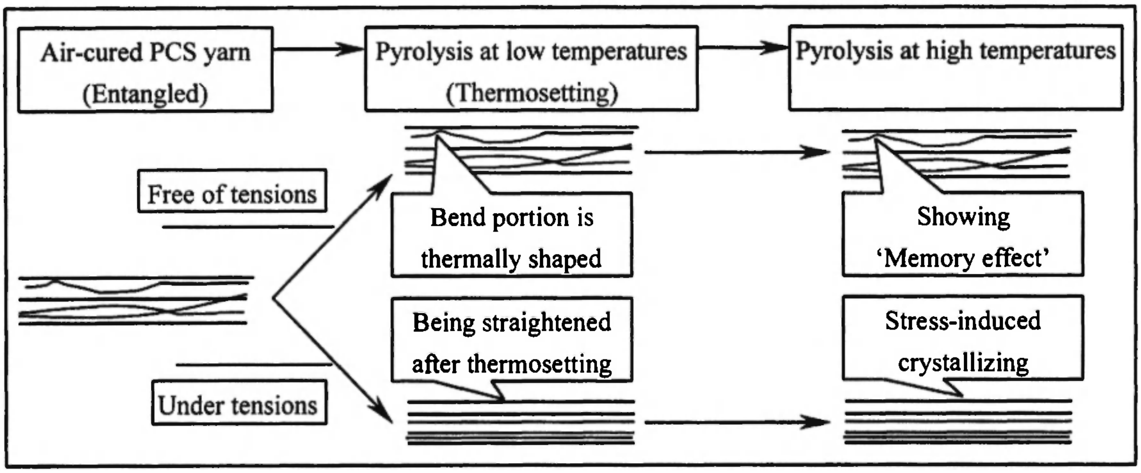

Fig.6: A proposed mechanism of the effect of firing tensions

The greatest impression from the above results is that the shrinkage could not be completely, or even suppressed to any large extent, otherwise filament will be broken. That is to say, under whatever conditions, zero-shrinkage could not be realized in the pyrolysis of PCS yarns.

However, for the air-cured PCS yarn whose average-shrinkage is 26%, the highest tensile strength and Young's modulus were obtained at the shrinkage close to 23%. Moreover, the highest value is about 12% higher than that of the freely shrunk SiC fiber (i.e. a controlled-shrinkage of 30% in Table 2).

Also, for the partially broken SiC fibers, axial cracks were usually detected through SEM analysis. Fig. 5 is a typical photo of this kind of flaw, which is the main reason for their much lower mechanical properties.

Regarding the improved mechanical properties of SiC fibers, information can also be obtained from the remarks in Table 2. When the shrinkage is lower than the maximum shrinkage, the yarns are straightened after pyrolysis, whereas the freely shrunk yarns are still in an entangled state, the same as their precursors' morphology. Also, due to the formation of axial cracks, the broken or partially broken yarns are in a much lower tensile strength than the freely shrunk yarns. Therefore, it may be inferred that straightened fibers are free of bend portions and may have a higher tensile strength if fewer axial cracks are formed on their surfaces. So, a controlled-shrinkage of 23% is necessary to obtain such a case and fibers obtained in this way have better mechanical properties.

Although shrinkage can be easily controlled as above, the technique is not suitable for the continuous preparation of SiC bundles and more importantly, the expanding property of the precursor is not utilized. The following section will discuss which specific tension is better to obtain the strongest SiC fibers, since this technique can be used in the continuous technology as already carried out for PAN-based carbon fibers.

4.3 Effect of specific firing tensions on the mechanical properties of SiC fibers

Fig. 3c and the published literature /2,9,10/ have told us that the mechanical properties of SiC fibers locate at lower level at temperatures below 800°C and climb immediately over 1000°C. Therefore, a uniform tension for the whole pyrolysis is not wise. Based on a statistical damage constituted model of a fiber bundle, a theoretical multi-step tension schedule has been carried out and will appear in detail elsewhere /11/. In that paper, average crack load of a precursor bundle was estimated when pyrolyzed up to a certain temperature and an up limit tension was also calculated on the condition that 99% of filaments survive.

However, that proposed tensile schedule is in 9 steps, each one corresponding to a ~100°C range. Thereby it must be simplified in application. Since 1000°C is a distinct temperature in view of the variation of tensile strength, we adopted a two-step tension schedule; one is from 200°C to 1000°C and the other from 1000°C to 1250°C. Also, we hold the opinion that a higher tension is preferable on condition that there are no new filaments broken. Mechanical properties of SiC fibers obtained under different firing tensions are shown in Table 3.

The results revealed that cracks occurred at 15cN/yarn for the air-cured PCS yarn, or partial breaking took place at 30cN/yarn for the pyrolyzed yarn up to 1100°C. Both of them are lower than the calculated values in the case of 99% fibers survival, which are 20cN and 100cN respectively according to the constituted model /11/. This may be because the filaments are not parallel to each other and/or some filaments have been broken before pyrolysis. Actually, the as-received cured PCS are entangled in curves, and

Table 3

Mechanical properties of SiC fibers obtained under different firing tensions

Specific tension, cN/yarn		Tensile strength, GPa	Young's modulus, GPa	Grain size*, nm
200-1000°C	1000-1250°C			
1	1	1.70	141	(amorphous)
5	1	1.77	145	(amorphous)
10	1	1.84	154	0.7
15	1	(Broken at 200°C)		
10	5	1.80	160	(amorphous)
10	10	1.88	168	0.8
10	15	1.85	169	0.7
10	20	1.94	180	1.1
10	25	1.90	186	1.3
10	30	(Partially broken at 1100°C)		

*From XRD analysis

in addition, more than 3% filaments have been broken just posterior to spinning /8/.

Tensile strength and Young's modulus are increasing with increase of firing tensions and more endurable tension means better mechanical properties. For example, with tension increasing from 1cN to 10cN at the first step, the tensile strength increased from 1.70GPa to 1.84GPa and the Young's modulus from 141GPa to 154GPa. These improved properties should be attributed to the thermoplastic nature and expanding property of the precursor, as already established from the shrinking behavior. Thus the tension tends to rearrange the filaments so that they are parallel to each other, providing the yarn with a straight morphology free of bend portions. Moreover, to some extent, the molecular structure of the precursor may be oriented along the longitudinal direction under this tensile stress and the enhanced crystallization may be such a result.

Unlike the tensile strength, which improved half during the first step and half during the second step, the Young's modulus improved more during the second step, from 160GPa to 186GPa, than during the first step, from 141GPa to 154GPa. This is related to the crystallization of SiC fibers obtained by this method, which changed from an amorphous state to a partially crystalline state of 1.3nm in grain size. The firing tension seems to induce the crystallization of β-SiC, which is in favor of both the tensile strength and the Young's modulus.

Overall, the optimal two-step tension schedule should be 10cN at 200-1000°C and 25cN at 1000-1250°C for this single PCS bundle. Taking account of both the two steps, an effect mechanism of firing tensions may be proposed, as shown in Fig. 6.

The as-received air-cured PCS yarn is entangled and curving. When pyrolysis is at low temperatures free of tensions, bend portions may be thermally shaped because further cross-linking will thermally occur on heating /2/. Therefore, these bend portions are retained after the final heat treatment with a macro morphology similar to that of its precursor yarn, or we may say SiC yarn obtained in this way inherits its parent's characteristics and shows a memory effect. These bend portions, as already pointed out by Yajima /3/, are the places where stress is concentrated and may act as the origin of failures when loaded.

When pyrolysis is under tension, however, the filaments are straightened to be parallel to each other by the thermosetting effect of the heat, using the expanding property of the precursor. SiC fibers obtained in this way should be somewhat lower in diameter after a certain elongation along the axis.

As far as the improved crystallization is concerned, creep should not be the real reason, as proved by the results of Simon /12/ and Bodet *et al.* /13,14/. Amorphous Nicalon fibers (NLP101) were found to creep at temperatures above 1000°C when loads were greater than a threshold and this stress threshold was found to decrease with temperature (0.3GPa at 1100°C and 0.17GPa at 1200°C)/12/. But the applied stress in the present case, ~0.03GPa (25cN), is obviously not large enough to creep the fibers. In fact, the loaded yarns were still shrinking, as opposed to creeping, when pyrolyzed above 1000°C. Therefore the most probable reason for the crystallization may be the stress-induced short-range ordering of SiC in addition to the molecular orientations at low temperatures, both of which, however, may need further intensive observations.

CONCLUSIONS

Pyrolysis is a conversion process from organic polymer to inorganic ceramic materials, during which mechanical properties changed remarkably. Shrinkage starts at about 540°C and the maximum shrinkage, 25-35%, differs greatly at different heating rates, namely, the higher the heating rate the higher is the shrinkage. The shrinkage could not be suppressed to any great extent, and if so, cracks and filament breaking would take place.

Firing tension has two ways to improve the mechanical properties of polymer-derived SiC fibers: 1) tension could straighten the entangled PCS yarns and ensure retention of a linear shape after the low-temperature thermosetting, 2) tension could slightly induce the crystallization of β-SiC. On further consideration of the endurable force for a 100 filament PCS bundle, a two-step tension schedule is suggested, that is, 10cN at 200-1000°C and 25cN at 1000-1250°C.

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