Melt Spun of Continuous Polycarbosilane Fibers

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ABSTRACT

The SiC fiber can be obtained by controlled pyrolysis of polymeric precursor such as polycarbosilane(PCS), which is first melted and spun so as to obtain so-called precursor fiber. This is converted to inorganic SiC by curing in air, heating in N_2 gas under tension. To prepare continuous polycarbosilane precursor fiber is one of the key technologies to prepare continuous SiC fiber. The relation between the polycarbosilane's characteristics and its spinnablity is studied in the present paper. Preparation conditions of continuous polycarbosilane precursor fibers such as the spinning temperature, spinning pressure, filter mode, air-flow receive mode and yarn's receive speeds, etc., are also studied.

I. INTRODUCTION

The continuous silicon carbide fiber is an important type of ceramic fiber. The fiber presents an attractive package of properties. They combine rather high strength and elastic modulus with high-temperature capability and a general freedom from environmental attack. These characteristics make it attractive as reinforcement in high temperature structural materials which have enormous application potentials in the aeronautics, aerospace and military fields and so on /1,2/. Japan has assumed a position of leadership in producing continuous SiC fiber under the trade name Nicalon /3,4/. Studies on fabrication and applications of SiC fiber have been carried out in our university since 1980.

The SiC fiber can be obtained by controlled pyrolysis of polymeric precursor such as polycarbosilane(PCS), which is first melted and spun to obtain so-called precursor fiber. This is converted to inorganic SiC by curing in air, heating to about 1250°C in N_2 gas under tension. To prepare continuous polycarbosilane precursor fiber is one of the key technologies for the continuous preparation of SiC fiber. The performances of the precursor fiber have a direct effect on the following processes and have an influence on the final performances of the SiC fibers .In this paper, polycarbosilane's spinnability, raw yarn's spinning process and conditions, etc., are studied.

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II. EXPERIMENTS AND MATERIALS

1. Polycarbosilane's (PCS) Synthesis

PCS is synthesized by the pyrolysis and rearrangement of polydimethylsilane /5/. PCS is a resin-like material. Its softening point is about 230°C.

2. Preparation of the polycarbosilane's raw yarns and continuous SiC fiber

PCS is melted in N_2 gas and according to certain temperature-gradient conditions rules in the ceramic precursor fiber melt spinning machine, the debubbled molten PCS is fed into the spinning assembly and is finally molded into precursor fibers with convergence and drawing. The precursor fibers are heaped in the special plate loosely and in certain conditions. PCS precursor fibers are become infusible fiber by means of heat treatment in air for some time under some temperature-gradient conditions. The infusible fibers are then treated at high temperature in N_2 gas under stretch in order to get continuous SiC fibers.

3.Analysis and Testing

(1) Molecular weight and its distribution: water-244 typed high performance liquid phase chromatograph, the solvent is toluene. (2) Melting point measurement: German HMK typed melting point measuring instrument. (3) Fiber diameter measurement: Optical reading microscope. (4) Fiber strength measurement: YG001 typed electronic strength instrument, the span is 20 mm, the speed of drawing head is 2mm/min.

III. RESULTS AND DISCUSSION

1. The relation between the polycarbosilane's melting point, molecular weight distribution and the spinnability

Compared with the drawing of general synthetic fiber, the drawing of polycarbosilane fiber is more difficult, which is demonstrated mainly in the following aspects: (1) molecular weight is relatively low, and there are more branched chains and crosslinked portions in the molecular structure. (2) Melt viscosity of the PCS is very sensitive to temperature. (3) The raw materials are brittle, melt strength of the PCS is very low, so precursor fiber is quite weak. (4) When leaving the spinning jet at about 0.5 cm, the raw yarns are solidified at once, the axial speed gradient is large.

PCS 's molecular weight and molecular weight distribution have quite a large influence on the spinnability. PCS with different melting points and molecular weight distributions is spun in relatively steady conditions, and the values of the ratio of continuous length and fiber diameter are used as the foundations of spinnability assessments. It can be seen from the experiments that the spinnability deteriorates when the dispersion coefficient of PCS is larger than 2.0, the spinnability is better as this coefficient is smaller than 2.0. The spinnability is better when the melting point decreases and it gets worse as the melting point and the molecular weight increases.

The GPC pattern of PCS can be divided into three portions of molecular weight zones with high, middle and low . The values of the corresponding size integral represent the contents of high and low molecular weights respectively. It can be seen that PCS's spinnability is obviously influenced when high molecular weight A_H/A_m and melting point increases, and that the spinnability is getting worse obviously as A_H/A_m is larger than 15%. PCS has excellent spinnability as the values vary within 5~13%.

2.Polycarbosilane' s purification and spinning pressure

Polycarbosilane for spinning must be purified in order to remove its impurities. The jet orifice may be clogged as there are impurities, so spinning pressure increases too fast, the shapes of liquid flows from the jet orifice change, thus resulting in yarns breaking and more blemishes. Their properties will become worse as SiC fibers are prepared from this kind of precursor fibers, and in serious cases, no threads will be formed due to too high pressure. By analyzing the PCS's synthesis process, it can be seen that the sources of impurities are as follows: (1) Because the temperatures in the autoclaves are too high, so small quantities of PCS near the autoclave's walls have been turned into particle-like inorganic substances, i.e. insoluble and infusible inorganic products. (2) Some crosslinked portions with higher molecular weights. (3) The corrosive products in equipment, air-borne dust particles, and solid particles and other kinds of impurity particles brought during operations. Experiments showed that polycarbosilane synthesis with combined filtering methods, and spinning with filtering method under metal nets, the purification results are all better, and the spinning pressure can also be normally controlled. Fig. 1 shows the changes of spinning pressures with three different filtering results but the same conditions in other respects. The first case is PCS which is not filtered with combined filtering methods when synthesized, the spinning pressures increase to greater values for a short time, so the PCS cannot be spun. The second case is a PCS which has been filtered but the filtering results are quite poor, this PCS can be spun into fibers, but the pressures increase quite fast, so the spinnability is obviously poorer than that of the PCS in the third case which is carefully filtered.

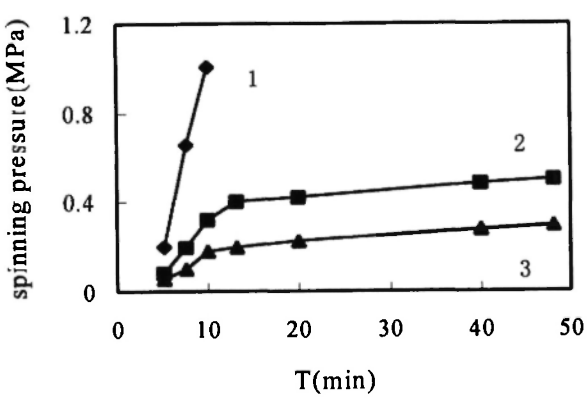

Fig. 1: The variation of spinning pressures with three different filtering results

In PCS melt spinning, bubbles are one of the main defects resulting in precursor fibers breakage. Because PCS molecular weight distributions have certain area, so the volatile components of the low molecular weight will be gasified as heated and minute bubbles will be produced, thus bringing about raw yarns breakage. Furthermore, the residual bubbles and other solid matters in fibers will result in structural defects in fibers, which notably reduces the mechanical properties of SiC fibers. We have used the debubbling method with reducing pressure, i.e.under melting state, the melt is stirred and meanwhile pressures are reduced. By using this method, the amount of bubbles decreases sharply, spinning jet plate is less clogged, and precursor fiber breakages are also markedly decreased.

3. Spinning temperature

The viscosity of polycarbosilane is strongly dependent on temperature. It is found from experiments that the spinnable temperature range for PCS is extremely narrow. Beyond this range, even if the temperature varies within 2~3°C, the viscosity may change greatly .Therefore, it is very important to control accurately the spinning temperature for the preparation of PCS precursor fibers. The determination of spinning temperatures is generally based on the size and the variation range of the PCS softening point.

Similarly, because the viscosity for PCS is strongly dependent on temperature, so accurate control of temperatures is of major importance to guarantee the homogeneity of fiber diameters. Fig. 2 gives the effects of temperatures on fiber diameters for some typed PCS as other conditions are not changed. The figure shows that fiber diameters increase as temperatures rise. This is because the rising temperatures reduce the viscosity 1 and make the melt flow faster when other conditions are not changed. It can be seen from Fig. 2 that even if the

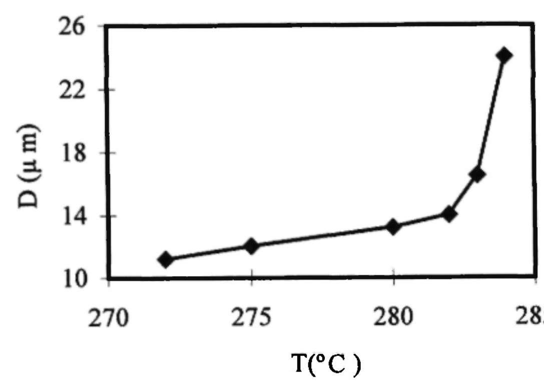

Fig. 2: The relation between spinning temperature and fiber diameter.

temperatures only vary 1°C, the fiber diameters vary at least about 4%, which shows that in addition to seriously controlling the yarn's receive speed and pump rate, it is also necessary to guarantee the discrete coefficients of the final fiber diameters within certain range. Reasonable spinning temperatures not only means proper temperatures and their control, but also means reasonable temperature matches among spinning pot, spinning blocks, jet plate, spinning cell, and surrounding temperature.

4.Fiber diameter and strength

To prepare continuous SiC fibers with high and uniform strength, PCS precursor fibers with smaller diameters and discrete coefficients and with less breakages must first of all be guaranteed. Figure 3 shows that the strength of such fibers decreases as its diameter increases.

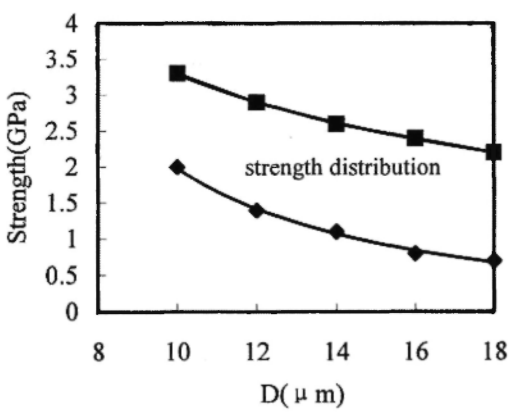

Fig. 3: Decrease in strength of the SiC fiber with increase in diameter.

IV. CONCLUSIONS

To prepare high performance and continuous SiC fibers, PCS precursor fibers with smaller diameters and discrete coefficients and with less spin breakages must first be guaranteed. As a brittle material, PCS precursor fibers are quite weak. Furthermore, their viscosity is strongly dependent on temperature. Comparing to the general chemical fibers, It is more difficulty to process PCS precursor fibers. PCS melting points and dispersion coefficients must be controlled strictly. By means of proper filtering and debubbling, the spinning temperatures and pressures, yarn's receive speeds and feeding rates must also be controlled accurately and matched reasonably, thus realizing continuous and steady spinning. The continuous PCS fibers heaped loosely and uniformly have been prepared for setting a good foundation for the preparation of continuous SiC fibers.

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