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Thermostatic Pyrolysis Process of Cured Polycarbosilane Fiber

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Abstract−As precursor fiber of advanced SiC fiber, cured polycarbosilane (PCS) fiber is prepared, and thermostatic pyrolysis of this fiber is studied in detail. Since the weight change is the most important characteristic of the pyrolysis degree of cured PCS fiber, a precise balance is applied on-line to follow the weight change of the cured PCS fiber, which was carried out in a standing style furnace. In thermostatic pyrolysis, the degree of pyrolysis, which is characterized by the weight loss of the fiber, and the properties of the final SiC fibers were found to be strongly dependent on the process conditions such as N_2 flow and the amount of fibers. From much evidence, it is the offgas evacuated in the process that plays an important role by accelerating pyrolysis and increasing pyrolysis degree.

Key words: Curing, Polycarbosilane Fiber, Thermostatic Pyrolysis, SiC Fiber

INTRODUCTION

As an advanced material, SiC-based fibers have been extensively developed and paid much attention since Yajima's pioneering work in 1975 [Yajima et al., 1978; Birot et al., 1996], the preparation of which follows five steps: 1) the synthesis of polysilane; 2) transfer polysilane to PCS at 450 °C; 3) spinning of the PCS precursor; 4) curing of PCS green fiber; 5) pyrolysis of the cured PCS fiber to SiC fiber [Soraru et al., 1990; Bunsell and Berger, 2000; Yajima et al., 1976]. During this process, the principal framework is changed from Si-Si, via Si-C, C-Si-O-Si, and finally transferred to SiC with oxidation content about 10%. And the last step is the key process for influencing the properties of the resultant inorganic fiber [Yajima et al., 1976; Cao et al., 2001; Hasegawa, 1989; Yajima et al., 1980] which is quite complex for the structure transfer, and the pyrolysis degree is hard to control. Thus, in this study, the isothermal pyrolysis of the cured PCS fiber is studied in detail and an interesting phenomenon is found.

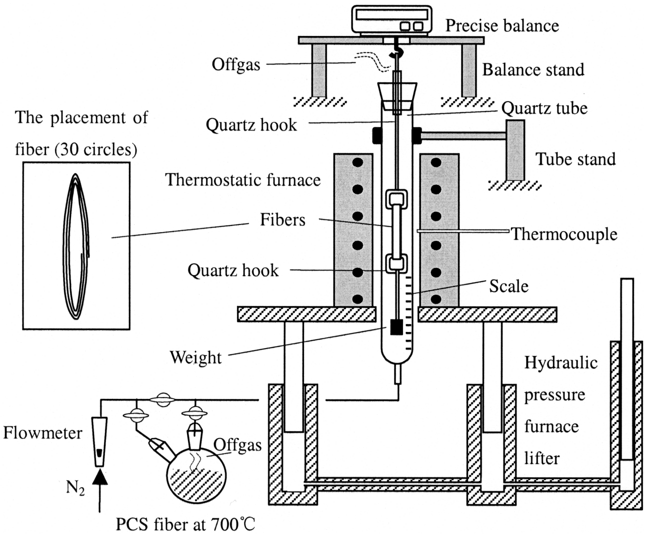

Fig. 1. The equipment measuring the weight and the shrinkage of cured PCS fibers in the thermostatic pyrolysis process.

EXPERIMENT

Based on Yajima's route [Yajima et al., 1980] and previous reports of our group [Feng et al., 1993], PCS with number average molecular weight 1250, was readily prepared by thermolysis of polydimethylsilane (PDMS) at 400 °C in N_2.

The resulting PCS was resolved in xylene, filtered and vacuum distilled to remove insoluble species and oligomer. The final golden-colored solid PCS with a softening point at 205 °C was melt-spun in N_2 into continuous fibers. The green fiber so obtained was cured at 170-190 °C in air atmosphere for 3 hrs, and thus a cured PCS fiber with the curing degree of about 81% was achieved. Then a certain amount (0.5 g) of the cured PCS fiber that was curled in circles (30 circles totally) was hung in a quartz hook, with a load to keep the fiber stretched. The furnace with a pre-set temperature was then raised from a lower position to a working position (as Fig. 1 shows) by hydraulic pressure lifter, and the fibers in the tube were heated up to the pre-set temperature in about 3 seconds. A balance with the precision of 0.001 g and a scale were used on-line to measure the weight loss and shrinkage of the fibers, respectively.

Tensile strength (TS) and elastic modulus of the SiC fiber were measured by using single filaments of length 25 mm at room temperature. Dual fibers were attached to paper tabs by using an adhesive and loaded in tension with spread speed of 0.5 mm/min until failure with a mechanical apparatus (Model 1122, Instron Corp., Canton). The gage length was 25 mm and at least twenty filaments were tested for each batch. To calculate tensile strength, Eq. (1) was used and fiber diameters (D) were determined with an optical microscope equipped with micrometer in an eyepiece. Modulus values were calculated without any corrections for the compliance of the mechanical testing system [Toreki et al., 1994].

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$$TS=load/D^2 \qquad (1)$$

Molecular weight of the precursor was determined by GPC (gel permeation chromatography, Waters) with s-Styragel columns calibrated with polystyrene standards and with THF as eluent at a flow rate of 0.5 ml/min.

The morphology of the fibers was studied by scanning electron microscopy (SEM) with a JSM-6300 (JEOL), and a seagull digital camera with the model of DF-4 was used for the macroscopic morphology of the fibers isothermally pyrolyzed at different temperatures. And the structure development was followed by infrared spectroscopy (BIO WIN RAD) in tablet mixed with KBr.

RESULTS AND DISCUSSION

The cured PCS fiber was pyrolyzed isothermally at different temperatures from 200 °C to 1,300 °C. The processes of the weight loss shown in Fig. 2 are similar to the result of Shimoo [Shimoo et al., 1994], which is finished in 5 minutes. Treated by first-order kinetics, the activation energy was found to be 29.3 kJ/mol, which is also similar to 31.7 kJ/mol reported by Shimoo [Shimoo et al., 1994].

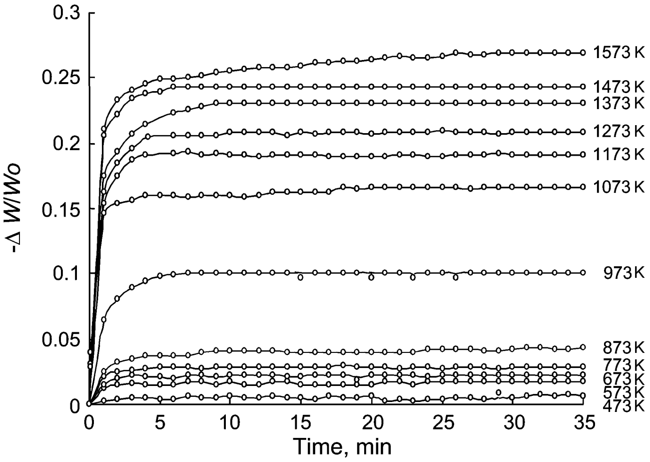

Fig. 2. The change of the weight loss rate of cured PCS during thermostatic pyrolysis from 473 K to 1,573 K.

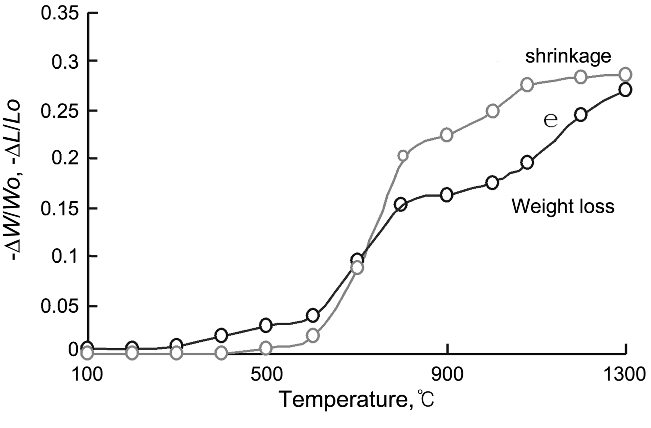

Fig. 3. The change of the weight loss rate and the shrinkage rate of the cured PCS fibers thermostatically pyrolyzed at different temperatures.

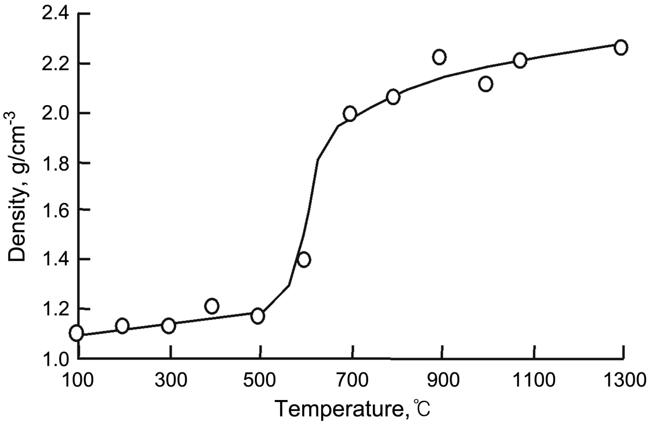

Fig. 4. The density of the cured PCS fiber thermostatically pyrolyzed at different temperatures.

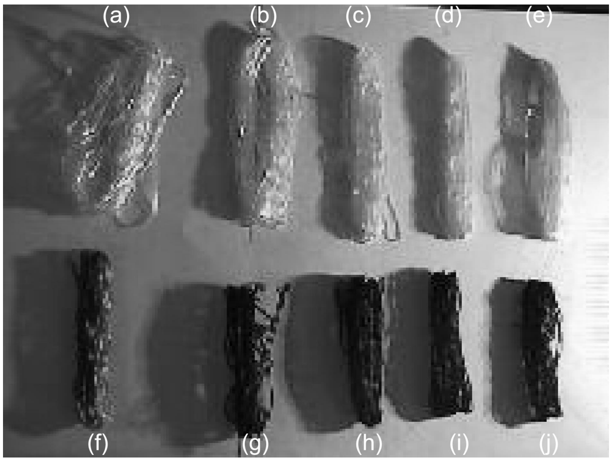

Fig. 5. The photos of cured PCS fibers thermostatically pyrolyzed at 200 °C (a), 300 °C (b), 400 °C (c), 500 °C (d), 600 °C (e), 700 °C (f), 800 °C (g), 900 °C (h), 1,000 °C (i), 1,100 °C (j).

For the isothermal pyrolysis of the cured PCS fiber, the weight loss and length shrinking (Fig. 3), density (Fig. 4), surface color (Fig. 5) and diameter (Fig. 6), there is a jump in the range of 600-800 °C which implies that the inorganic process happened mainly in this range. This is also proved by the IR spectra (Fig. 7) which shows that the peaks of Si-H (2,100 cm^{-1}), C-H (2,950 cm^{-1}, 1,410 cm^{-1} and 1,360 cm^{-1}), Si-CH3 (1,250 cm^{-1}), -OH (3,500, 3,600 cm^{-1}) decreased, and nearly disappeared when the temperature reached 600 °C. While the peak of Si-O (1,030 cm^{-1}) likely increased before 600 °C, and when the temperature is higher than 600 °C, the Si-O peak decreased again and nearly disappeared when the temperature was higher than 1,200 °C.

The thermostatic pyrolyzed fibers were finally heat treated with the following program: from room temperature to 500 °C in 3 hrs and hold for 1hrs, increased to 900 °C within 6 hrs, then to 1,300 °C in 3 hrs, finally dropped to room temperature in half an hour. The relationship of the thermostatic temperatures with the tensile strength and modulus of the final SiC fibers is shown in Fig. 8, which implies that during the two-step method for the preparation of SiC fiber, the final fiber has higher tensile strength when the pre-pyrolysis temperature is set at ca. 700 °C and 1,000 °C.

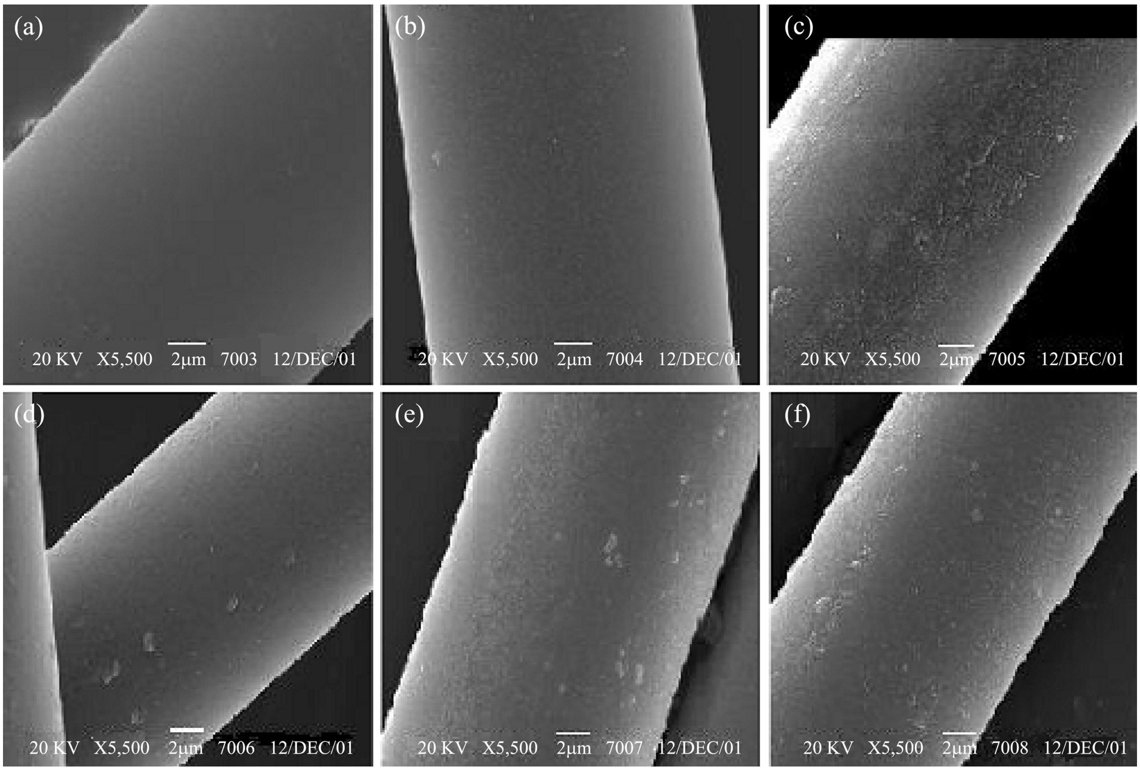

Fig. 6. SEM of cured PCS fibers thermostatically pyrolized at 500 °C (a), 600 °C (b), 700 °C (c), 800 °C (d), 1,100 °C (e), 1,300 °C (f).

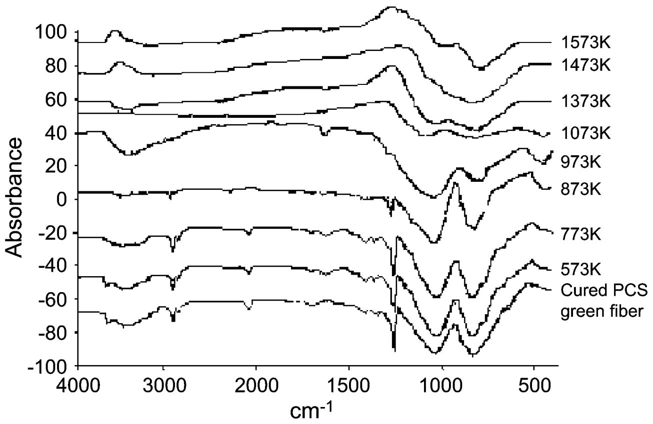

Fig. 7. IR spectra of the cured PCS fibers thermostatically pyrolized at different temperatures.

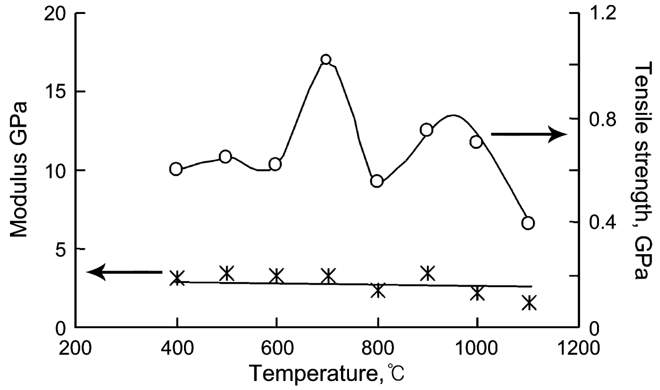

Fig. 8. The relationships between SiC fibers' property and the first step thermostatic pyrolysis temperatures.

Table 1. The final weight loss rate of cured PCS fiber thermostatically pyrolyzed at 600 °C with various amounts of fibers in different flow rates of nitrogen

Amount of fiber (circle)	N_2 flow (ml/min)			
	60	100	150	200
10	2.68	5.50	3.04	2.85
20	3.67	6.20	3.22	3.43
30	4.88	8.56	3.75	3.72

When different amounts of the cured PCS fibers were pyrolyzed isothermally at 600 °C with various N_2 flow, an interesting phenomenon was found. Normally, the weight loss and shrink are strongly dependent on various conditions, such as the flow rate of the nitrogen and the amount of fiber, since the N_2 brings out of the offgas, the weight loss is expected to be higher when the flow rate of the nitrogen is increased, considering the fibers have less chance to adsorb the offgas. However, when the N_2 flow is higher than 100 ml/min, the opposite fact was found (shown in Table 1).

From Table 1, one can also find that increasing the amount of the fiber leads to higher weight loss when flow rate of nitrogen is constant. Fig. 9 shows that increasing the amount of fiber or decreasing the flow rate of nitrogen turns the fiber darker. The explanation is that the fiber's re-adsorption of offgas leads to a higher weight loss because lower N_2 flow or larger amount of fiber should be in favor of the re-adsorption. However, when the N_2 flow is too small, e.g. 60 ml/min, the weight loss is hindered by the gas-release

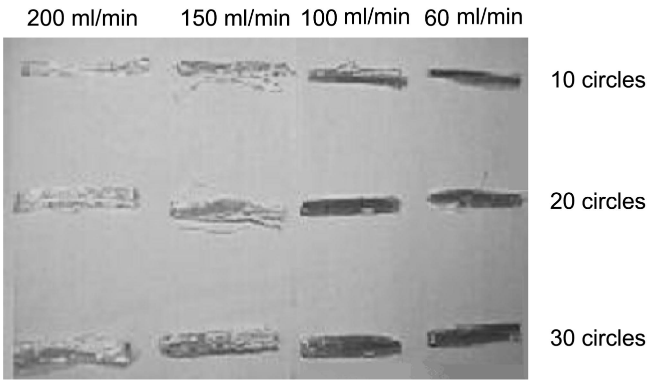

Fig. 9. **The cured PCS fibers thermostatically pyrolyzed at 600 °C for 35 minutes with different flow rates of nitrogen and different amounts of fibers.**

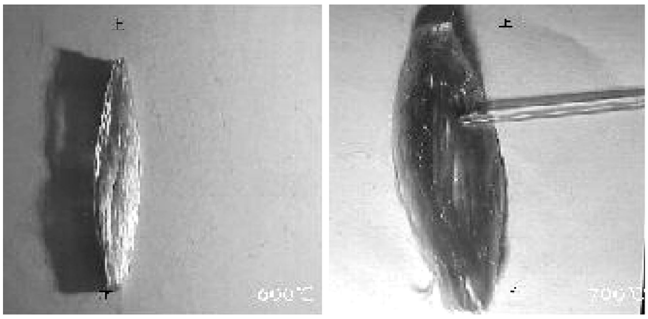

Fig. 10. **The cured PCS fiber thermostatically pyrolyzed at 600 °C (left) and 700 °C (right) for 35 minutes (the flow rate of nitrogen is 150 ml/min).**

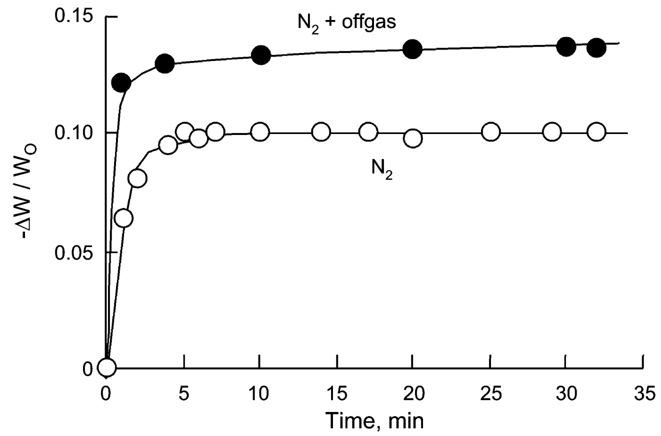

Fig. 11. **The weight loss of cured PCS fibers thermostatically pyrolyzed at 700 °C in different atmosphere.**

reactions. Some more visible evidence can be drawn from the samples as in Fig. 10. The color in the upper part of the fiber is darker than that in the lower part (see left), and the inner part is darker than that of the outer part (see right). Considering the N_2 flows from the bottom of pyrolyzing tube, the upper part must adsorb more offgas, while the inner part, where the offgas is more difficult to diffuse out, the fibers there adsorb more offgas.

It seems the offgas accelerates the pyrolysis reaction, or the more the fiber adsorbs the offgas, the more it reacts and some more offgas is released. A more direct evidence of this effect was achieved with the apparatus shown in Fig. 1, from which the original nitrogen was mixed with offgas. The results are as expected to compare the rates of the weight loss (Fig. 11) and the colors of the resulted fibers (Fig. 12). To reveal the reaction mechanism, more work should

Fig. 12. **The photos of cured PCS fibers heat treated at 700 °C (left, in pure nitrogen; right, in nitrogen and offgas).**

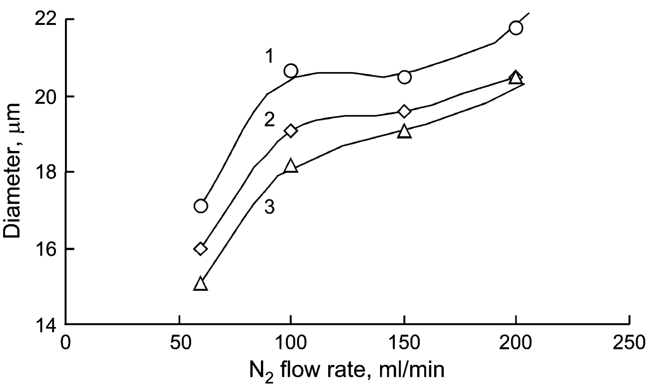

Fig. 13. **The relationship of the flow rate of nitrogen and diameter of cured PCS fibers heated at 600 °C.**
(1) 10 circles; (2) 20 circles; (3) 30 circles

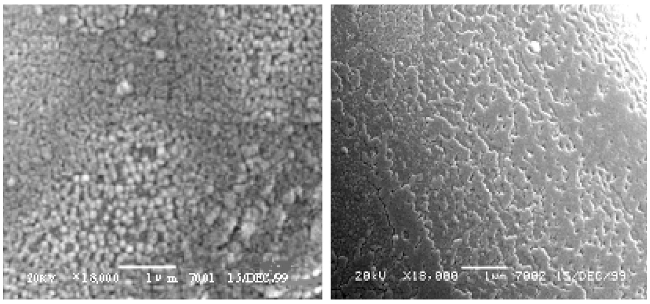

Fig. 14. **The SEM images of the cured PCS fibers thermostatically pyrolized for 35 min at 700 °C (left, in pure nitrogen; right, in mixture of nitrogen and the offgas).**

be done.

The offgas from the pyrolysis of preceramic polymer not only accelerates the process, but also deteriorates the property of the remaining materials. From Fig. 13, the SiC fibers produced at lower flow rate of the nitrogen or larger amount of fiber resulted in a thin diameter, or the fiber was whittled by the effect of offgas. This can also be demonstrated by the SEM observations in Fig. 14, where the offgas made the fiber more porous and coarse and the related tensile strength of the final fiber was lower to a ratio of 30% than that of the fiber from pure nitrogen.

CONCLUSION

In thermostatic pyrolysis of the cured PCS fiber, the inorganic process happened mainly from 600-800 °C and the weight loss finished in about 5 minutes. Treated by the kinetics of first-order reaction, the activation energy was found to be 29.3 kJ/mol. And increasing the amount of fiber or decreasing the N_2 flow will result into a higher weight loss and lower tensile strength for the final SiC fiber. It is the offgas evacuated in the process that played an important role by accelerating pyrolysis and increasing the degree of weight loss. Also, for the two-step method for preparing SiC fiber, the final fiber has higher tensile strength when the pretreated temperature is 700 °C or 1,000 °C.

ACKNOWLEDGMENT

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