Mechanical properties and microstructural fracture behaviors of dry-spun SiC fibers

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Abstract
Research and development of SiC/SiC composite materials as structural members of aerospace engines is progressing. In order to manufacture SiC/SiC composites with excellent high-temperature characteristics, the SiC fibers which have high mechanical properties at high temperature are necessary; thus, further development of SiC fibers is considered a critical issue. In addition, the development of low-cost SiC fibers is necessary for the practical application of SiC/SiC composites. Here, the low-cost SiC fibers can be fabricated by dry spinning method. In the dry-spinning method, the raw material, Polycarbosilane (PCS) is dissolved in an organic solvent and the solution is spun at room temperature. As high-molecular-weight Polycarbosilane is prepared in advance, the infusible process conventionally required in the melt-spinning method is not required. In this study, to evaluate the differences among dry-spun SiC fibers fabricated under various conditions, monofilament tensile tests were conducted. Examination of the fracture surface and elemental analysis of arbitrary cross-sections were then performed to investigate the effects of the fabrication conditions. The tensile strength results indicated that defects were suppressed by excluding low-molecular-weight components and that heat treatment between 1300°C and 1500°C resulted in the maximum strength. Weibull analysis revealed that the dry-spun fibers exhibited lower tensile strength but smaller variation of fiber strength than that of the melt-spun fiber because the dry-spun fibers were more homogeneous. However, evaluation of the crystallinity indicated that the interference pattern derived from the crystal was unclear in the dry-spun fibers but clear in the melt-spun fiber. Therefore, it was suggested that the dry-spun fibers exhibited lower crystallinity than the melt-spun fiber. In addition, the dry-spun and melt-spun fibers exhibited similar C/Si ratios, whereas a large amount of oxygen was detected on the surface of the dry-spun fiber relative to that on the surface of the melt-spun fiber. Further improvement of the mechanical properties is expected upon increasing the molecular weight of the raw material and improving the microstructure.

Keywords: SiC fiber, Dry-spun fiber, Dry-spinning method, Tensile strength, Weibull distribution, Fracture surface observation, Crystallinity evaluation

1. Introduction
In the aviation industry, the demand for aircraft engines with lower fuel consumption has recently increased because of fuel cost increases and CO₂ reduction requirements. One of the main means of improving the fuel efficiency of aircraft engines is to improve their thermal efficiency by weight reduction of the structural members and the use of a higher-pressure ratio. Therefore, the application of SiC/SiC composites, which are ceramic matrix composites (CMCs),
has increased (Alijaz, et al., 2013) (Katoh, et al., 2014). A CMC is a material that exhibits improved high fracture toughness owing to fiber reinforcement. SiC/SiC composites are lightweight and exhibit excellent heat resistance. For example, the density of SiC/SiC composites is approximately 1/4 to 1/3 of those of conventional nickel-based superalloys with 20% higher heat-resistant temperatures (Shibayama and Takahashi, 2000) (Naslain, 2003). Therefore, SiC/SiC composites are expected to be applied not only in aircraft engines but also for further applications in the future (Tamura, et al., 2007).

Hi-Nicalon Type-S (Nippon Carbon Co., Ltd.) is a SiC fiber that is currently in practical use. This fiber is produced by melt spinning and an electron-beam infusibilization process of a precursor polymer. Therefore, Type-S fiber exhibits excellent mechanical properties even under high-temperature environments (Hasegawa, et al., 2000) (Naslain, 2004). However, these processes are associated with high costs, and it is thus necessary to reduce the manufacturing costs (Ichikawa, 2006). Therefore, SiC fibers prepared using the dry-spinning method have been developed. In the dry-spinning method, a high-molecular-weight raw material is dissolved in organic solvent and spun at room temperature; thus, there is no need for the melting or infusibilization processes. However, because dry-spun fibers have only been developed over a short period, the optimum fabrication conditions have not yet been determined; therefore, these fibers are not yet used in practice.

In this study, to determine appropriate fabrication conditions for dry-spun fibers, the effects of the heat-treatment temperature and precursor molecular weight on the resulting dry-spun SiC fibers were investigated. After determining the mechanical properties of dry-spun fibers prepared under different fabrication conditions, the relations between the fabrication conditions and the fracture behavior and composition were investigated.

2. Experimental procedure
2.1 Materials

In this study, dry-spun fibers (IA-X) and melt-spun fibers (Type-S) were used. The dry-spun fibers were fabricated through the process of dry spinning of raw material, Polycarbosilane (PCS), first heat-treatment (1000°C, H2/Ar atmosphere) for decarburization and second heat-treatment (Ar atmosphere). On the other hand, the melt-spun fiber requires the melt spinning process and the electron beam irradiation infusibilization process.

For the IA-X fibers, two types of PCS, ordinary PCS and PCS excluding the low-molecular weight components (High-PCS) were used, and the second heat-treatment temperature ranged from 1300°C to 1500°C. Conditions A and B used ordinary PCS treated at 1300°C (A) and 1500°C (B). Conditions C, D, and E used High-PCS treated at 1300°C (C), 1400°C (D), and 1500°C (E). These fiber conditions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Table 1 SiC fibers in this study</th>
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<tbody>
<tr>
<td>Type-S</td>
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<tr>
<td>IA-X</td>
</tr>
<tr>
<td>A</td>
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<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
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* private information

2.2 Monofilament tensile strength test and Weibull analysis

To determine the mechanical properties of the SiC fibers, monofilament tensile tests were performed using a universal testing machine (Shimadzu, Autograph AG-100 NPlus, Shimadzu). The cross-head speed was 2.0 mm/min, and the gauge length was 25 mm. After measuring the fiber diameter from the interference phenomenon of the laser light, the fiber was held along the load axis. After cutting both sides of the mount, the tensile test was started. To prepare the fracture surfaces, glycerin was dropped on the fiber surface and paper cut to an appropriate length was placed around the specimen.

The Weibull function shown in Eq. (1) was used to evaluate the mechanical properties and variation of fiber strength. In Eq. (1), σ0 is a scale parameter, which is a representative value of the strength; m is the Weibull factor, which represents the deflection of the strength; V is the volume of each specimen, V0 is the average volume; and P(σ) is
the cumulative fracture probability, which was calculated using the median rank method, as expressed in Eq. (2). Here, \( i \) is the serial number and \( n \) is the number of specimens.

\[
P(\sigma) = 1 - \exp \left[ -\frac{V}{V_0} \left( \frac{\sigma}{\sigma_0} \right)^m \right]
\]

(1)

\[
P(\sigma) = \frac{i - 0.3}{n + 0.4}
\]

(2)

2.3 Observation of the fracture surface and surface conditions

To investigate the microstructural fracture behaviors, fracture surface samples obtained from the tensile tests were examined using field-emission scanning electron microscopy (FE-SEM; S-4500S, Hitachi) at an acceleration voltage of 15 kV.

2.4 Crystallinity evaluation and elemental analysis

To evaluate the crystallinity and elemental composition of the fibers, structural observation was performed using field-emission scanning transmission electron microscopy/energy-dispersive X-ray spectrometry (FE-STEM/EDX; JEM-2100F, JEOL). The crystal size and elemental distribution were determined using FE-STEM. A thin sample with a thickness of 100 \( \mu \)m or less was prepared for the FE-STEM analysis using focused ion beam (FIB) milling (JIB-4000, JEOL). After carbon coating the fiber surface, the sample was irradiated with a gallium-ion beam to scrape the surroundings, finally obtaining the target sample. From the grain size and elemental composition results, the effects of the fabrication conditions were determined.

3. Results and discussion

3.1 Fiber characteristics

The mechanical properties, Weibull parameters, and fiber diameters are summarized in table 2. In table 2, the values in ( ) means the standard deviation. Representative stress–strain curves are presented in Fig. 1 and the tensile test results are arranged as Weibull plots in Fig. 2. First, comparing the fiber diameter of IA-X and Type-S, the diameters of IA-X was smaller, and the variation of diameter was also small. This result likely occurred because in the dry-spinning method, the precursor was dissolved in organic solvent so, the spinnability was improved. Moreover, in the dry spinning method, the temperature change during the spinning is small, and this is thought to affect the spinnability. The reduction of the fiber diameter has the advantage that the fiber volume content can be increased when applying SiC fibers to a CMC and the supple fiber can improve the weaving ability.

When comparing the dry-spun fibers for both precursor conditions, ordinary PCS and High-PCS, the scale parameters that represent the strength of the fiber changed with the heat-treatment temperature. When the second heat-treatment temperature was increased from 1300°C to 1500°C, the scale parameters of the IA-X fibers prepared from ordinary PCS decreased by 17%, whereas the IA-X fibers prepared from High-PCS decreased by only 9%. This result suggests that by excluding the low-molecular-weight components from the precursor, fiber deterioration resulting from over heat treatment could be reduced. In addition, a higher second heat-treatment temperature resulted in a higher elastic modulus. Next, for the system of dry-spun fiber made from High-PCS, the IA-X-D fiber treated at 1400°C exhibited the highest scale parameter and Weibull factor. Furthermore, although the strength of the IA-X-D fiber did not reach that of the Type-S fiber, its variation of strength was smaller than that of the Type-S fiber. These characteristics were further examined by investigating the fracture behaviors and crystallinities, as shown below.
Table 2 Characteristics of SiC fibers

<table>
<thead>
<tr>
<th></th>
<th>Fiber diameter $d_0$ [µm]</th>
<th>Scale parameter $\sigma_0$ [GPa]</th>
<th>Weibull factor $m$</th>
<th>Elastic modulus $E$ [GPa]</th>
</tr>
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<tbody>
<tr>
<td>Hi-Nicalon Type-S</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>13.5(1.60)</td>
<td>3.60</td>
<td>4.55</td>
<td>317</td>
</tr>
<tr>
<td>B</td>
<td>8.42(0.34)</td>
<td>2.27</td>
<td>3.61</td>
<td>242</td>
</tr>
<tr>
<td>C</td>
<td>7.94(0.59)</td>
<td>1.89</td>
<td>3.17</td>
<td>266</td>
</tr>
<tr>
<td>D</td>
<td>10.8(0.93)</td>
<td>2.38</td>
<td>4.42</td>
<td>238</td>
</tr>
<tr>
<td>E</td>
<td>10.2(0.76)</td>
<td>2.40</td>
<td>5.36</td>
<td>258</td>
</tr>
<tr>
<td></td>
<td>9.58(0.26)</td>
<td>2.18</td>
<td>4.95</td>
<td>291</td>
</tr>
</tbody>
</table>

(a) Type-S and IA-X_A and B fibers
(b) IA-X_C, D, and E fibers

Fig. 1 Representative stress–strain curves obtained from monofilament tensile tests showing the dependence of the mechanical properties on the fabrication conditions. The melt-spun fiber, Type-S (white), exhibited the highest tensile strength and elastic modulus. Among the dry-spun fibers, the IA-X_D fiber (orange) made from High-PCS and treated at 1400°C exhibited the highest mechanical properties.

(c) Type-S and IA-X_A and B
(d) IA-X_C, D and E fibers

Fig. 2 Monofilament tensile strength test results arranged in a Weibull plot. The IA-X_D (orange) fiber prepared from High-PCS treated at 1400°C exhibited the smallest variation of fiber strength, and the Weibull factor of the IA-X_D fiber was superior to that of the melt-spun fiber, Type-S.

3.2 Fracture behaviors and surface conditions

To investigate the fracture behaviors, the fiber fracture surfaces were examined using FE-SEM. The fracture surfaces are shown in Fig. 3. For all the fibers, typical brittle failure with characteristic mirror and hackle patterns was observed. In the IA-X_A, B, and C fibers, obvious defects were observed. However, no obvious defects were observed in the IA-X_D and E fibers. Therefore, it is suggested that exclusion of the low-molecular-weight component from the precursor was effective in suppressing defects, and in this system, heat-treatment temperatures between 1300°C and 1500°C resulted in the maximum fiber strength.

In addition, to investigate the cause of the small variation of fiber strength, high-magnification examinations of the mirror zone and surface conditions of each fiber were performed. The results for the mirror zone are presented in Fig. 4, and the surface conditions are shown in Fig. 5. The results indicate that the dry-spun IA-X_D fiber had a smoother structure than the melt-spun fiber, Type-S; for this reason, the dry-spun fiber was considered to exhibit excellent reliability of fiber strength (small variation of fiber strength). However, the relaxation of the stress concentration resulting from the smooth surface led to an improvement in the strength; however, the Type-S fiber exhibited the
highest strength. Therefore, the difference in strength is thought to be attributed to other factors in addition to the difference in microstructure.

Fig. 3 FE-SEM images of fiber fracture surfaces. Typical brittle fracture surfaces with mirror and hackle patterns are observed for all the fibers. The IA-X_A, B, and C fibers had obvious defects, whereas the Type-S and IA-X_D and E fibers had no obvious defects.

Fig. 4 High-magnification FE-SEM images of mirror zone of Type-S and IA-X_D fibers. The IA-X_D fiber made from High-PCS and treated at 1400°C had a denser and more aligned structure. This dense and aligned structure was thought to contribute to the high reliability of fiber strength of the IA-X fiber.

Fig. 5 FE-SEM images of surfaces of Type-S and IA-X_D fibers. An irregularity was observed on the surface of the Type-S fiber, whereas the surface of the IA-X_D fiber had a smooth structure. This smooth structure was thought to contribute to the high reliability of fiber strength of the IA-X fiber.
3.3 Crystallinity evaluation

To evaluate the crystallinity of the fibers, microstructural observation using FE-STEM was performed. Using TEM, it is possible to investigate the crystallinity from the interference pattern derived from the crystal structure. The results are presented in Fig. 6. The observation point was near the fiber surface. Comparing the IA-X_A and IA-X_B fibers, when the second heat-treatment temperature increased from 1300°C to 1500°C, the interference pattern derived from the crystals became clear. Therefore, it was suggested that crystallization progressed with increasing second heat-treatment temperature. As described above, an increase in the elastic modulus with increasing second heat-treatment temperature was confirmed; this finding appeared to be resulted from the crystals, which were more rigid than the amorphous structures, growing with increasing second heat-treatment temperature.

In addition, when comparing the IA-X_D fiber, which exhibited the highest strength among the dry-spun fibers, with the Type-S fiber, the interference pattern of the Type-S fiber was clearer than that of the IA-X_D fiber. Therefore, the Type-S fiber was considered to exhibit higher crystallinity, which explains why the strength of the IA-X_D fiber could not reach that of the Type-S fiber. However, the strength of the IA-X_E fiber treated at 1500°C was inferior to that of the IA-X_D fiber. Therefore, the simple increase in the crystallinity with increasing second heat-treatment temperature does not lead to an improvement in strength. It was considered that the presence or absence of the infusibilization process (that is, the molecular weight of the precursor) was also involved as a factor of strength improvement.

3.4 Elemental analysis

The results of the elemental analysis are presented in Fig. 7. The elemental analysis was conducted for the Type-S and IA-X_D fibers. The horizontal axis represents the distance from the outermost surface of the fiber, and the vertical axes represent the C/Si ratio and oxygen concentration. In both fibers, the carbon content was larger at the surface side, and in the interiors, the Type-S and IA-X_D fibers had the same elemental compositions. However, the IA-X_D fiber contained more oxygen near the surface. The presence of a large amount of oxygen causes deterioration of the mechanical properties at high temperature; therefore, it is necessary to reduce the amount of oxygen from the dry-spun fiber. The reasons why the large amount of oxygen was detected in IA-X were thought to be that the raw material of IA-X contained larger amount of oxygen than that of Type-S, and that the pyrolysis reaction expressed in Eq. (3) (Shimoo, et al., 1992) did not progress sufficiently in IA-X_D treated at 1400°C. In Eq. (3), as the progress of reaction, the oxygen contained in amorphous is consumed, that is, the oxygen remains without the progress of the pyrolysis reaction.

\[
\text{SiC}_{1+x}O_y \text{(amorphous)} \rightarrow \beta\text{-SiC(s)} + \text{SiO(g)} + \text{CO(g)}
\]  

4. Conclusions

In this study, the conclusions are as follows.

1. The exclusion of low molecular weight component was thought to lead to the suppression of defects.
2. In the dry spinning method, it was possible to fabricate fibers with dense and aligned internal structure and smooth surface structure. This resulted in the high reliability of fiber strength.
3. With the increase of second heat-treatment temperature, the crystallization progressed, resulting the increase of elastic modulus.
4. It was suggested that crystallinity affected the fiber strength.
5. In the dry-spun fiber, a large amount of oxygen was detected. Since oxygen causes the deterioration of mechanical properties at high temperature, the reduction of oxygen is necessary for the dry spinning method.
Fig. 6 Interference patterns derived from crystallinity obtained using FE-STEM. When comparing the IA-X_A and IA-X_B fibers, the interference pattern derived from the crystallinity was clearer for the IA-X_B fiber; therefore, the crystallinity improved upon increasing the second heat-treatment temperature. In addition, the Type-S fiber exhibited high crystallinity and thus it showed high strength.

Fig. 7 Elemental analysis of Type-S and IA-X_D fibers. For both fibers, the C/Si ratio showed the same trend, and a large amount of carbon was detected at the surface. However, for the IA-X_D fiber, a large amount of oxygen was detected on the surface.

References


