Degradation Mechanism of Amorphous Silicon Carbide Fiber due to Air-Exposure at High Temperatures

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The degradation mechanism of the amorphous silicon carbide fiber, Tyranno-ZMI®, exposed in air at 1173 ~ 1873K for 20ks were studied. The average strength of the bare fiber, which was prepared by etching away the oxidation layer on the fiber surface, decreased with increasing exposure temperature, especially when exposed at the temperature higher than 1673 K. The measurement of the crystallite size of β-SiC in the fiber with Sherrer method revealed that coarsening of the crystalline occurred in the fiber exposed at the temperatures higher than 1773 K. The scanning electron microscope observation of the fiber surface showed that the many defects formed on the fiber surface. By introducing an artificial notch directly into the fiber specimens using a focused-ion(Ga⁺)-beam, the fracture toughness values of the as-supplied fiber and of the fiber exposed at 1673 and 1773 K were determined to be 1.8 ± 0.3, 1.9 ± 0.4 and 1.3 ± 0.4 MPa√m, respectively. Based on these results, the reason for the degradation of the fiber was attributed to the extension of the surface defect which was enhanced by the reduction in fracture toughness due to coarsening of the β-SiC crystalline.

(Received October 16, 2006; Accepted November 30, 2006; Published January 25, 2007)

Keywords: silicon carbide fiber, fracture toughness, fracture strength, artificial notch, degradation

1. Introduction

SiC/SiC composites are one of the most promising materials for high temperature structural applications such as power generation and advanced jet engines, and for fusion structural applications.1–3) For description of the mechanical behavior is considered to be strongly affected by the fracture toughness of the fiber. Thus, it is very important to clarify whether fracture toughness of the fiber affected by high temperature air-exposure or not. Fracture toughness of amorphous SiC fibers in the as-fabricated state has been determined successfully the fracture toughness of polycrystalline SiC fiber, Tyranno-SA® batch grade 3 whose diameter was 7.5 µm on average. Such a method is a useful tool to estimate the fracture toughness of fibers, and was applied also in this work to measure the change of fracture toughness of the exposed fiber.

Recently, the authors have developed a method to introduce an artificial notch into small diameter fibers using focused-ion(Ga⁺)-beam.13) With this method, they determined successfully the fracture toughness of polycrystalline SiC fiber, Tyranno-SA® batch grade 3 whose diameter was 7.5 µm on average. Such a method is a useful tool to estimate the fracture toughness of fibers, and was applied also in this work to measure the change of fracture toughness of the exposed fiber.

The aim of the present work is to clarify the degradation mechanism of the amorphous SiC fiber without oxidation layer from the fracture morphology observation and measurement of the fracture toughness value.

2. Experimental Procedure

The amorphous SiC fiber, Tyranno-ZMI® (hereafter noted simply as the fiber for convenience) used for the present study was fabricated by Ube Industries Ltd.2) It was prepared by the use of polyzirconocarbosilane (PZC) which was synthesized by the reaction between polycarbosilane and zirconiumacetylacetonate at 573 K.6) PZC was continuously synthesized.
melt-spun and then cured in air by heating up to 443 K. By pyrolysis at 1573 K of the cured PZC fiber, it was obtained. The /C12-SiC crystals formed in the process are around 2 nm in size. The fiber diameter is 11 μm. The fiber-specimens had the sizing agent on the surface in the as-supplied condition. In advance, the sizing agent was removed by the heat treatment in air at 873 K for 1.8 ks. Then the fibers were exposed in air at 1173 K for 20 ks. As stated above, due to air-exposure at high temperatures, the oxidation reaction layer (SiO₂) formed on the fiber surface. In order to measure the fracture toughness of the fiber itself, the bare fiber without SiO₂ layer was prepared by etching away the SiO₂ with HF + NH₄F (5:1 molar ratio) solution at 303 K for 1.8 ks.

To investigate the crystal size change caused by the air-exposure, powder X-ray diffractometry (RINT2000, Rigaku, Tokyo, Japan) was applied. The apparent size d of the /C12-SiC crystals was determined using the Sherrer’s equation given by eq. (2) with a full width at half maximum (FWHM) of /C12-SiC (111) diffraction peak,

\[
d_{111} = \frac{1.0 \lambda}{\beta \cos \theta}
\]

where λ is the X-ray wavelength, θ is the diffraction angle and β is the FWHM.

In the present work, Mode I notch (straight-fronted edge notch as shown schematically in Fig. 2) was introduced into fiber test specimens using a focused-ion beam (hereafter noted as FIB for convenience) micromachining method. The details of the procedure are shown elsewhere. The fiber diameter D and notch depth a of each test specimen for fracture toughness determination were measured with a scanning ion microscope (SIM) attached to the FIB apparatus (JFIB-2300, JEOL, Tokyo, Japan).

Tensile test for the notched and unnotched monofilament fibers was carried out at a crosshead speed of 8.3 × 10⁻⁶ m/s at room temperature with a universal tensile testing machine (MMT-10N-2, Shimadzu Co., Kyoto, Japan). 30 fiber specimens were tested for each condition and the result was averaged. The test was carried out in glycerin in order to prevent the segmentation of the fiber upon fracture. Thus, the original fracture surface could be obtained for observation. The load was monitored with a 2.5 N load cell.

The morphology of the exposed fiber surface and fracture surface of fibers were observed with a Field Emission-Scanning Electron Microscope (FE-SEM) (X-500, Toshiba Co., Tokyo, Japan).

3. Results and Discussion

3.1 Fiber strength

Figure 3 shows the measured average fracture strength of unnotched fiber without the oxidation layer for a gage length 10 mm, σf,un plotted against exposure temperature, T. The average strength of the as-supplied fibers was 3.74 GPa. It decreased with increasing exposure temperature; 3.70, 3.57, 1.77 and 0.50 GPa for exposure at 1173, 1473, 1673 and 1773 K.

3.2 Structural change in exposed fiber

Figure 4 shows the crystallite size observed from /C12-SiC (111), d₁₁₁ plotted against exposure temperature, T.
As already reported, the as-supplied fiber contains β-SiC crystals. In the present work, the size was measured to be 2.5 nm, being comparable to the reported value of 2 nm. When the fiber was exposed at the temperatures higher than 1673 K, the size grew significantly with increasing exposure temperature. On the other hand, the measured integrated intensity of β-SiC (111) diffraction peak did not vary as shown in Fig. 5, in which the integrated intensity of the exposed fiber is normalized with respect to that of the as-supplied value. Therefore, it is judged that coarsening of the β-SiC crystalline took place within the present experimental condition. It was speculated that such a microstructural change in the fiber affects on the fracture toughness. Then, the fracture toughness of the as-supplied fiber and of the fiber exposed at 1673 (beginning stage of coarsening) and 1773 K (coarsened stage) was determined, whose result is shown below.

3.3 Determination of fracture toughness

3.3.1 Observation of an artificial notch and fracture surface of the artificially notched fiber

Figure 6 shows the appearance of (a) as-supplied unnotched and (b) artificially notched fiber. The notch tip radius was 25 nm on an average (c).

An example of the fracture morphology of the notched fiber is presented in Fig. 7. The mirror, mist and hackle zones are clearly found, which demonstrates that the fiber fracture initiated at the notch introduced by the present FIB method. a and D in Figs. 6 and 7 are the notch depth and the fiber diameter, respectively.

3.3.2 Fracture toughness of the fiber

To determine the fracture toughness, it is necessary to determine experimentally the fracture strength of notched fiber $\sigma_F$, notch depth $a$ and fiber diameter $D$. Furthermore, correction factor $Y$ derived from shape of the notch is also needed. According to our former work, the correction factor for the present straight-fronted edge notch is given as a function of $(a/D)$ by

$$Y\left(\frac{a}{D}\right) = 0.99 - 0.61 \left(\frac{a}{D}\right) + 5.66 \left(\frac{a}{D}\right)^2 - 0.16 \left(\frac{a}{D}\right)^3$$

and fracture toughness value $K_{IC}$ is expressed by

$$K_{IC} = Y\left(\frac{a}{D}\right) \cdot \sigma_F \sqrt{\pi a}$$

Substituting the measured values of $\sigma_F$, $a$ and $D$ and calculated value of $Y\left(\frac{a}{D}\right)$ into eq. (4), we had $K_{IC}$-value.

Figure 8 shows the unified fracture strength $Y\left(\frac{a}{D}\right) \cdot \sigma_F$ of the as-supplied fiber specimens with an artificial notch (a), and that of the notched fiber specimens exposed at 1673 K (b) and 1773 K (c) plotted against notch depth $a$, together with the calculation results for $K_{IC} = 1.0 \sim 2.5$ MPa $\sqrt{m}$ based on eq. (4). The dash-dotted line and broken lines show average tensile strength of unnotched fibers and those of standard deviations, respectively.

In the case of as-supplied fiber, all of the measured fracture strength values were lower than the unnotched fiber strength,
and the \( Y[a/D] \cdot \sigma_f \)-values decreased with increasing \( a \) (Fig. 8(a)). This result indicates that the fibers were fractured by the artificially introduced notch. Therefore, the \( K_{IC} \) value was estimated from all of the tested specimens.

In the case of the fiber exposed at 1673 K, as it is difficult to distinguish whether the fiber test specimens are fractured by inherent defects or by the introduced notch in the range of small notch size \( (< 0.7 \, \mu m) \), the \( K_{IC} \) value was estimated from the fiber test specimens which fractured at lower than

Fig. 6 Appearance of the side surface of (a) as-supplied fiber, (b) notched fiber and (c) notch area at high magnification, where \( a \) is the notch depth and \( D \) is the fiber diameter.

Fig. 7 An example of the fracture morphology of the as-supplied fiber with an artificial notch, where \( a \) is the notch depth and \( D \) is the fiber diameter.

Fig. 8 Unified fracture strength \( Y[a/D] \cdot \sigma_f \) of the (a) as-supplied fiber specimens with an artificial notch, and that of the notched fiber specimens exposed at (b) 1673 K and (c) 1773 K plotted against notch depth \( a \), together with the calculation results for \( K_{IC} = 1.0 \sim 2.5 \, MPa \sqrt{m} \) based on eq. 4.
1.3 GPa (average unnotched strength: 1.77 GPa, standard deviation: 0.31 GPa). In the range of large notch size, the fracture strength decreased with increasing \( a \), so that all data in the large notch size region ( \( > 0.7 \mu m \) ) were used for fracture toughness estimation.

In the case of the fiber exposed at 1773 K, unnotched fiber strength was too low to distinguish whether the fiber test specimens are fractured by inherent defects or by the introduced notch in the whole range of the notch size. Therefore, the fracture morphology of all of the notched fiber test specimens were examined with an optical microscope (X2F-NR type A, Nikon Co., Tokyo, Japan) in order to check whether fracture was caused by the artificially introduced notch or not. Then, the \( K_{IC} \) value was estimated from the fiber test specimens which were fractured by the introduced notch. Such fibers are indicated with the dark circles in Fig. 8(c).

The estimated fracture toughness values of the as-supplied fiber and of the fiber exposed at 1673 and 1773 K were 1.8 \( \pm \) 0.3, 1.9 \( \pm \) 0.4 and 1.3 \( \pm \) 0.4 MPa\( \sqrt{\text{m}} \), respectively.

Figure 9 shows the determined fracture toughness of the fiber \( K_{IC} \) plotted against exposure temperature \( T \), together with the aforementioned average fracture strength of unnotched fiber \( \sigma_{F,un} \) and crystallite size of \( \beta\text{-SiC} \) \( d_{111} \). The correspondence of the change of fracture toughness value to that of the crystalline size is good. This result accounts for the experimental result; fracture toughness of the fiber exposed at 1673 K was nearly the same with as that of the as-supplied fiber, but that of the fiber exposed at 1773 K was decreased.

### 3.4 Degradation mechanism of the fiber itself

Figure 10 shows the morphology of the side surface of the fiber; (a) as-supplied, (b) exposed at 1673 K and (c) exposed at 1773 K. The defect formed on the fiber surface. It grows with increasing exposure temperature. The fractograph of the bare fiber exposed at 1673 K obviously indicated that the fiber fracture originated from such defect, as shown in Fig. 11.

Generally, fracture strength of fibers with surface defect can be expressed by eq. (5) by using equivalent defect size \( C_{Eq,s} \):

\[
\sigma_F = \frac{K_{IC}}{1.12\sqrt{\pi C_{Eq,s}}} \quad (5)
\]

As the fracture toughness value \( K_{IC} \) has been obtained, the equivalent defect size of unnotched fibers can be estimated by eq. (5').

\[
C_{Eq,s} = \frac{1}{\pi} \left( \frac{K_{IC}}{1.12\sigma_F} \right)^2 \quad (5')
\]
Eq,s-values of as-supplied fiber and the fiber exposed at 1673 and 1773 K were estimated to be 60, 290 and 1700 nm, respectively.

In the case of 1673 K, the $K_{IC}$ did not decrease from the original value, but the defect formed on fiber surface. Accordingly the reason for the reduction in fiber strength is attributed to the formation of the defect on the surface whose equivalent size is 290 nm. On the other hand, in the case of 1773 K, the $K_{IC}$ decreased and also surface defect formed. Thus the reason for the degradation of the fiber was attributed to the extension of the surface defect which was enhanced by the reduction in fracture toughness due to coarsening of the $\beta$-SiC crystalline.

If the $K_{IC}$ value of the fiber exposed at 1773 K does not decrease from $K_{IC} = 1.9 \text{MPa}\sqrt{\text{m}}$, fracture strength of the fiber calculated by eq. 5 for the estimated equivalent crack size $C_{Eq,s}$ ($= 1700 \text{nm}$) becomes 0.73 GPa. However, in practice, the $\sigma_F$ value was 0.50 GPa, and that of as-supplied fiber was 3.74 GPa. Then, the ratios of contribution of the formation of surface defect and the reduction in fracture toughness to the overall degradation are attributed to 93 and 7%, respectively.

4. Conclusions

The degradation of the amorphous silicon carbide fiber, Tyranno-ZMI®, exposed in air at 1173 ~ 1873 K for 20 ks were studied. Main results are summarized as follows.

(1) The average strength of the fiber, whose oxidation layer was etched away, decreased with increasing exposure temperature, especially at the temperatures higher than 1673 K.

(2) Coarsening of $\beta$-SiC crystalline occurred in the fiber exposed at the temperature higher than 1773 K.

(3) By introducing an artificial notch directly into the fiber test specimens using a focused-ion(Ga$^+$)-beam, the fracture toughness of the as-supplied fiber and of the fiber exposed at 1673 and 1773 K were determined to be $1.8 \pm 0.3, 1.9 \pm 0.4$ and $1.3 \pm 0.4 \text{MPa}\sqrt{\text{m}}$, respectively.

(4) The reason for the degradation of the fiber was attributed to the extension of the surface defect which was enhanced by the reduction in fracture toughness due to coarsening of the $\beta$-SiC crystalline.

Acknowledgments

The authors wish to express their gratitude to JSPS (Japan Society for the Promotion of Science) for the support of this work.

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