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Fabrication of transparent continuous oxynitride glass fiber-reinforced glass matrix composite

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Unidirectional-aligned continuous SiCaAlON fiber-reinforced glass matrix composites have been fabricated and their light transmittance was measured. Optically transparent composites with the fiber volume fraction from 0.03 to 0.10 were fabricated by a hot-pressing method. The light transmittance of the composite perpendicular to the fiber axis in the wavelength range from 200 to 700 nm was measured, and found to decrease with the increase of the fiber volume fraction. This decrease is explained by the theory proposed by the authors (HI and YK). The major source of a light transmittance loss of the composite originates from a phase change of transmitted light in the composite.

1. Introduction

The incorporation of continuous ceramic fibers into glass materials has been shown to improve the strength and fracture resistance of the materials [1–4]. However, the light transmittance of glass materials at visible wavelengths disappeared after incorporation of the fiber into the glass matrix because of the poor light transmittance of the fiber. This non-transparent property of the composite limits its application fields even though high strength and high fracture resistance are added to the glass materials.

To overcome this problem, the authors recently reported the possibility of fabrication of optically transparent short oxynitride glass fiber-reinforced glass matrix composites [5–7]. It was clear, however, that the maximum efficiency of the reinforcing fiber was obtained by the incorporation of continuous fibers. Therefore, if optically transparent continuous fiber-reinforced glass matrix composite is obtained with a small loss of the light transmittance of a glass matrix, the composite was expected to open new application fields. The potential of the composite has not yet been reported, however. The aim of this paper is to show the possibility of fabricating optically transparent continuous fiber-reinforced glass matrix composite.

2. Experimental procedure

Optically transparent continuous oxynitride fiber (SiCaAlON fiber, Shimadzu Corp., Kyoto, Japan) was used as a reinforcement material [7]. The continuous fiber with a diameter ($2R_f$) of 20 μm was supplied in a form of 100 fibers per unit bundle. Before slurry infiltration into the fiber bundle, the fiber was fully cleaned with acetone to remove the starch coating of the fiber. SiO_2 (31 mol %)-B_2O_3 (36 mol %)-BaO (18 mol %)-La_2O_3 (15 mol %) glass powder with an average diameter of 25 μm was used as a matrix. Table I lists properties of the fiber and matrix [7, 8].

Fig. 1 illustrates the fabrication process of the composite. The matrix glass powder was mixed with water to form a slurry. The cleaned oxynitride fiber bundle was made to pass through the slurry and then dried by heated air. The glass-adhered fiber bundle was then wound uniformly onto a drum to obtain prepreg tape. The prepreg tape was dried, cut and aligned unidirectionally, and put into a boron-nitride coated steel die. Then, the prepreg sheet was set on hot-pressing equipment, preheated in air at 773 K for 0.72 ks and heated to 1003 K with a heating rate of 50 K/min. The temperature of the steel die was measured by a chromel-almel thermocouple embedded in the side of the die. When the temperature reached 1003 K, the temperature was held for 0.3 ks without applied pressure to achieve uniform temperature distribution. After the holding, a pressure of 50 MPa was applied to the prepreg tape by a press and the pressure was again held for 60 min. The hot-pressed composite was then cooled to room temperature at a rate ≈ -5 K/min. The fabricated composite was removed from the die when the temperature reached room temperature ($\approx$297 K). For the purpose of comparison, a monolithic matrix glass was also fabricated under the exactly the same processing temperature-time schedule. In this case, the glass powder was put directly into the steel die and hot-pressed.

The fiber volume fraction was varied by controlling the amount of glass powder used during preparation

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TABLE I Some properties of the fiber and matrix

	SiCaAiON fiber	Matrix
Coefficient of thermal expansion, $\alpha(\times 10^{-6}\ K^{-1})$	7.7	7.9
Refractive index, n_D ($\lambda = 589.3$ nm)	1.704	1.704
Young's Modulus, E (GPa)	130	60
Room temperature strength (MPa)	3000–5000 [a]	30–40 [b]

[a] Tensile strength.
[b] Three point flexural strength with a specimen of $50 \times 50 \times 3$ mm (thick) with a span length 30 mm.

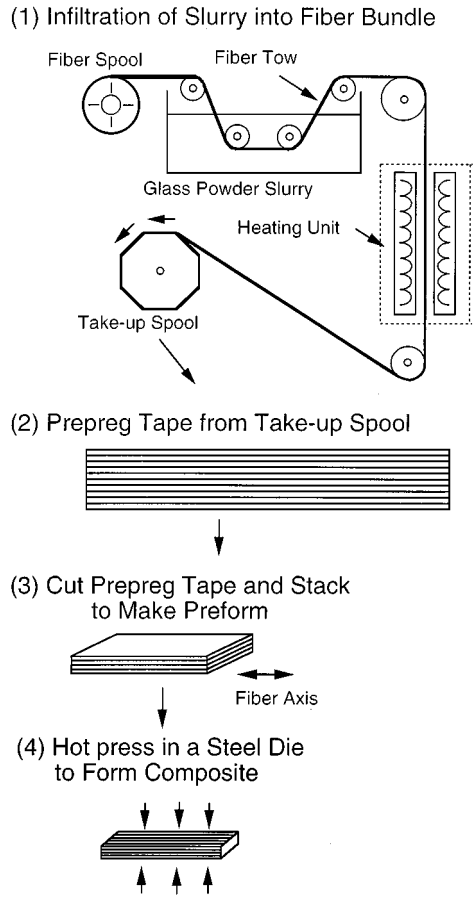

Figure 1 Schematic illustration of the fabrication process of the composite.

of the slurry. The actual fiber volume fraction of each composite, however, was identified individually by determining the total fiber area in the transverse cross-sectional area of the specimen under an optical microscope. Typical thickness of the hot-pressed composite and monolithic glass matrix was ≈1.5 mm with the fiber volume fraction of ≈0.03, 0.05, and 0.1. The microstructure of the composite was observed under reflective light and cross-polarized transmission light using a conventional optical microscope (BUH, Olympus Co., Ltd., Tokyo, Japan).

The surfaces of the as fabricated composites perpendicular to the pressing direction were progressively polished with a conventional metallurgical procedure. Final polishing of the surfaces was done by 1.1 μm diamond paste. The thickness of the specimen for the measurement of light transmittance was 1.0 mm (±0.1 mm). This means that the surface of the composite perpendicular to the fiber axis was used for light transmission measurement.

The light transmittance of the polished specimen at a wavelength range from 200 to 700 nm with the area ≈100 mm^2 was measured by a transmission optical spectrometer (UV-3100PC, Shimadzu Corp., Kyoto, Japan) at a fully controlled temperature of 297 K (±1 K). Resolution of the spectrometer for the wavelength range used was less than 0.1 nm.

The light transmittance of the monolithic matrix glass and bulk fiber were also measured. The specimen and the procedure were completely identical to those of the composite specimen.

3. Results and discussion

Fig. 2 shows the typical appearance of the monolithic glass matrix and composites (thickness ≈1 mm) with their fiber volume fraction, f. Characters underneath each monolithic glass matrix and composite are legible through these specimens. This evidence indicates that both the matrix and the composites have optical transparency in the visible wavelength region. However, as clearly seen in the photograph, the light transmittance of the composite seems lower than that of the monolithic matrix and the light transmittance of the composite decreases with increase in the fiber volume fraction. The hair-line appearance of the composite, shown in Fig. 2, is related to the differences of the light transmittance of this local high and low volume fraction region. More uniform fiber distribution is required to obtain full light transmittance of the composite by modification of the preparation process of the prepreg tape and glass matrix flaw during the hot-pressing.

Fig. 3 shows the light transmission spectra of the monolithic glass matrix, fiber, and composites. The light transmittance of the fiber is nearly zero at the wavelength shorter than ≈280 nm. This is natural because the glass material for the fiber has a strong inherent absorption below this wavelength. Above ≈280 nm, the transmittance increases with increase in the wavelength up to ≈77% and the transmittance saturates at λ ≈400 nm. The light transmittance of the monolithic glass matrix continuously rises with the increase in wavelength and the rate of increase changes at wavelength ≈350 nm. At a wavelength longer than 300 nm, the light transmittance of the composite gradually increases. Fig. 4 shows the plots of the normalized light transmittance of the composite, $\langle T_c \rangle$, at λ = 589 nm (Na-D ray) versus fiber volume fraction, f. Here, the light transmittance of the composite, T_c, is normalized by the light transmittance of the monolithic matrix glass, T_m, at the same wavelength, i.e.,

$$\langle T_c \rangle = \frac{T_c}{T_m}. \quad (1)$$

The light transmittance of the monolithic glass matrix is also plotted as $f = 0$. The figure suggests that the light transmittance of the composite decreases rapidly with the increase in fiber volume fraction.

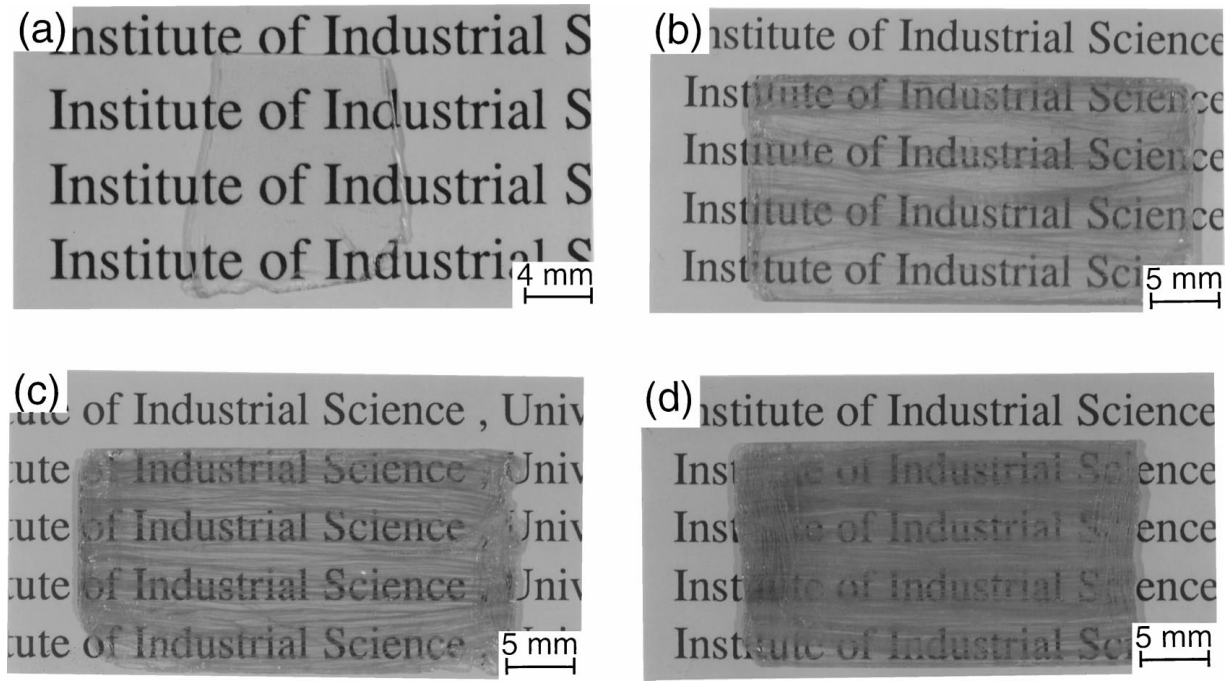

Figure 2 Appearance of the hot-pressed glass matrix (a) and composites (b) $f = 0.03$, (c) $f = 0.05$, (d) $f = 0.10$.

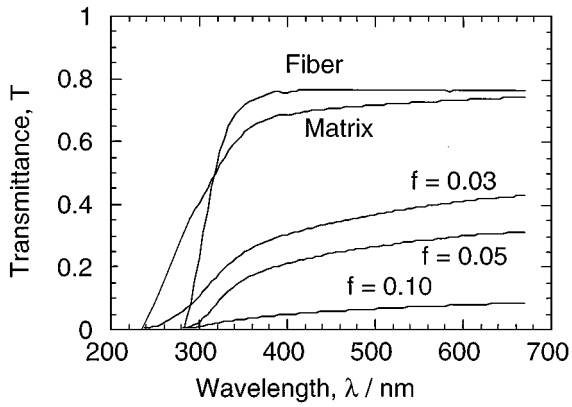

Figure 3 Light transmission spectra for the fiber, matrix, and composite.

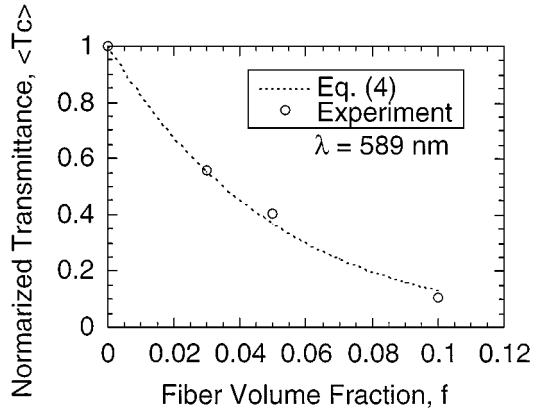

Figure 4 Plots of the normalized light transmittance of the composite, $\langle T_c \rangle$, versus fiber volume fraction, f, at $\lambda = 589$ nm.

In general, light attenuation in solid materials is usually discussed with the Rayleigh scattering, (the fiber radius, $R_f \gg \lambda$), Rayleigh-Gans-Debye scattering ($R_f \approx \lambda$), and/or Mie scattering (R_f is comparable in size or a little larger than the wavelength) [9–11]. The light transmittance of the monolithic glass matrix, T_m, for monochromatic light* is given by [12]

$$T_m = \left[1 - \frac{\left(n_m^0 - n_a\right)^2}{\left(n_m^0 + n_a\right)^2}\right]^2 \exp(-\alpha d) \qquad (2)$$

where α is the loss factor, d is the thickness of the specimen, n_m^0 is the refractive index of the monolithic matrix ($n_m^0 = 1.704$), and n_a is the refractive index of air (1.000 [13]). The slightly lower value of the light transmittance of the monolithic matrix glass than the prediction by Equation 2 ($T_m = 0.869$) indicates the existence of micro-scale light scattering sources in the hot-pressed monolithic matrix glass. However, obtained T_m and α indicate that the effects of this micro-scale light scattering of the matrix phase ($\approx$1 mm) are assumed to be quite small on the light transmittance of the thin composite.

In this experiment, the diameter of the fiber ($2R_f = 20\ \mu$m) is much larger than the wavelength of light at visible wavelength region ($R_f \gg \lambda$). In such case, the light scattering by the existence of the fiber is an important factor to reduce light transmittance. Recently, Iba and Kagawa [14] showed the theoretical form of the light transmittance of a continuous fiber-reinforced composite with $(n_f^c - n_m^c) \ll 1$ and with $R_f \gg \lambda$, where n_f^c and n_m^c are the refractive indices of the fiber and matrix in the composite, respectively. This theory successfully explained the light transmittance of continuous glass fiber-reinforced epoxy matrix composites [14]. The theory concludes that the major factor of the light extinction in an unidirectionally reinforced composite

* Hereafter, the refractive indices and the light transmittance at $\lambda =$ 589 nm are used.

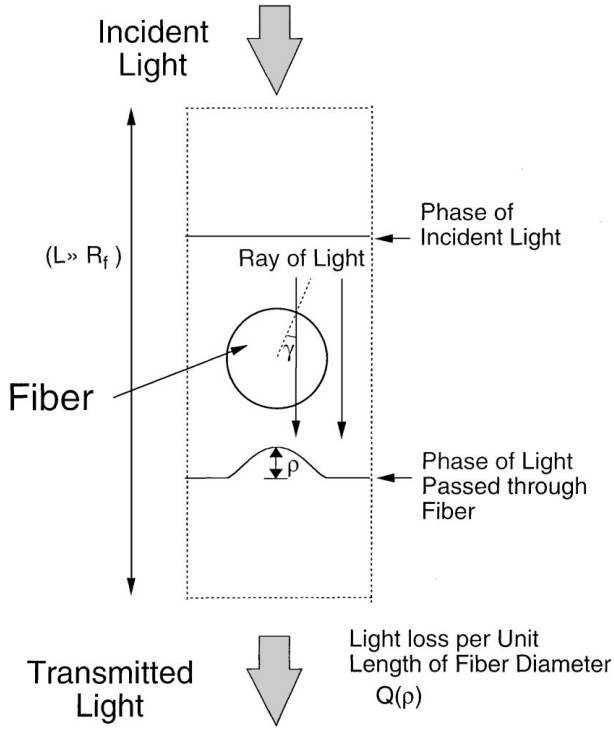

Figure 5 Light attenuation model in an unidirectionally aligned continuous fiber-reinforced composite.

is the accumulation of phase shift of a light when the light pass through the composite.

The refractive indices of the fiber and matrix after fabrication differ from those of raw materials by a thermal misfit strain [15]. The approximate value of thermal misfit strain, ε^{T}, is given by

$$\varepsilon^{\mathrm{T}} \approx \int_0^{\Delta T} (\alpha_{\mathrm{f}} - \alpha_{\mathrm{m}})\, dT \qquad (3)$$

where α_{f} and α_{m} are the coefficients of thermal expansion of fiber and matrix, respectively, ΔT is the temperature difference between the stress free temperature and room temperature. Here, the stress free temperature is assumed to be the same as the processing temperature. In this experiment, the thermal expansion coefficient of the fiber and matrix, respectively, are 7.7×10^{-6} and $7.9 \times 10^{-6}\,\mathrm{K}^{-1}$. The misfit strain estimated from Equation 3 using $\Delta T = 700$ K is $\approx 1.4 \times 10^{-4}$. This value is small enough to cause large changes in $n_{\mathrm{f}}^{\mathrm{c}}$ and $n_{\mathrm{m}}^{\mathrm{c}}$ from their initial values: the change of $(n_{\mathrm{f}}^{\mathrm{c}} - n_{\mathrm{m}}^{\mathrm{c}})$ is an order of 10^{-4}. The condition of the Iba-Kagawa theory ($(n_{\mathrm{f}}^{\mathrm{c}} - n_{\mathrm{m}}^{\mathrm{c}}) \ll 1$ and $R_{\mathrm{f}} \gg \lambda$) is satisfied in this study.

According to the theory [14], the light transmittance of the unidirectional continuous fiber-reinforced composite perpendicular to fiber axis, $\langle T_{\mathrm{c}} \rangle$, is given by

$$\langle T_{\mathrm{c}} \rangle = \left(1 - 2Q_{\mathrm{ext}}(\rho)\sqrt{\frac{f}{\pi}}\right)^{\frac{d}{R_{\mathrm{f}}}\sqrt{\frac{f}{\pi}}} \qquad (4)$$

and

$$Q_{\mathrm{ext}}(\rho) = 2\rho \int_0^{\pi/2} \sin(\rho \cos\gamma) \sin^2\gamma\, d\gamma \qquad (5)$$

where Q_{ext} is an extinction function [9], γ is the angle of incidence to fiber, and ρ is $2\pi(n_{\mathrm{f}}^{\mathrm{c}} - n_{\mathrm{m}}^{\mathrm{c}})R_{\mathrm{f}}/\lambda$. Fig. 5 shows a light attenuation model for a fiber in a unidirectionally aligned fiber-reinforced composite. This theory assumes that the major light loss during light transmittance in the unidirectional continuous fiber-reinforced composite is due to phase shift of light passed through the fibers with the refractive index different from that of surrounding matrix under a condition of $(n_{\mathrm{f}}^{\mathrm{c}} - n_{\mathrm{m}}^{\mathrm{c}}) \ll 1$ and $R_{\mathrm{f}} \gg \lambda$. The calculated results are normalized by $T_{\mathrm{m}} (\approx 0.869)$ and the results are shown in Fig. 4 by broken line ($2R_{\mathrm{f}} = 20\ \mu$m, $(n_{\mathrm{f}}^{\mathrm{c}} - n_{\mathrm{m}}^{\mathrm{c}}) = 0.0032$,[†] and $d = 1.0$ mm are used for the calculation). This agreement between the experiment and theory confirms that the light transmittance loss is due to accumulation of a phase shift slightly enlarged by misfit strain when a light passes through the fibers.

4. Concluding remarks

The present results demonstrate the possibility of fabricating a new type of optical-base continuous glass fiber-reinforced glass matrix composite. However, preliminary study of mechanical evaluation of the composite reveals that the maximum achieved three-point bend strength of the composite is $\approx$50 MPa ($f = 0.03$). This strength level is nearly the same order as that of a monolithic glass material fabricated by the same hot-pressing condition. Controlling both optical and mechanical interface properties while keeping the expense of light transmittance low is the key to improving the mechanical properties of this composite.

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[†] The value of this parameter also includes errors by the anisotropy of thermal misfit strain, geometrical factors such as fiber wearing and misalignment of the fiber axis.

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