Crystallization Behavior of High Purity Amorphous Silicon Nitride Fiber

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高純度非晶質窒化ケイ素繊維の結晶化挙動

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The crystallization of high purity polymer-derived amorphous Si_3N_4 fiber was investigated. The amorphous Si_3N_4 fiber was heat-treated (1400, 1425, 1450, 1475 and 1500°C, for 1-100h in N_2), and the crystallinity was estimated from X-ray diffraction patterns. Hexagonal crystalline particles growing on the surface of the fiber were observed by SEM. The crystallization seems to proceed by the vapor phase growth mechanism, in which SiO vapor takes part as silicon carrier between amorphous fiber and crystalline particles. While BN powder was used as a powder bed, the crystallization and grain growth were retarded and crystalline particles were grown inside the fiber. In this case the crystallization seems to proceed by the solid phase growth mechanism. The activation energies were calculated for heat treatment with and without BN powder and found to be about 1273 and 602 kJ/mol, respectively. Durability of Si_3N_4 fiber at 1300 and 1400°C was estimated.

Key-words: Amorphous, Silicon nitride fiber, Polysilazane, Crystallization, Activation energy

1. Introduction

The properties of silicon nitride, for example, resistance to thermal shock, corrosion, creep and oxidation, continue to generate interest in its application as high-temperature structural material, and an insulating diffusion mask in electric devices. Dense sintered silicon nitride has excellent high-temperature strength, high-electrical resistivity, low coefficient of thermal expansion, and low density relative to other high-temperature ceramics and superalloys, but these sintered silicon nitride contains impurity, which takes part as sintering agent, such as Y_2O_3 ¹⁾ or Al_2O_3 ,²⁾ etc. Therefore the sintered silicon nitride has not been representing the intrinsic properties of silicon nitride.

Recently considerable attention has been directed to the use of inorganic polymers as precursors to high-temperature and high-performance ceramics such as Si_3N_4 . Some of the potential advantages in the preparation of ceramic materials from these precursors include as follows:⁶⁾ (1) improved compositional homogeneity in the product because of mixing of elemental components in the molecular

and atomic levels, (2) high-purity ceramic products with uniform, small-grained microstructures, (3) the ability to produce high-surface area powders of controlled morphology and (4) the preparation of refractory ceramics at relatively low temperatures. Furthermore, the solubility and fluidity of inorganic polymers afford potential processing routes to binders, sintering aids, thin films and fiber. Thin films and fiber are often difficult or impossible to produce by the more traditional ceramic processing techniques.

Perhydropolysilazane (PHPS), produced by Tonen Corporation,³⁾ is an inorganic polymer as precursor for Si_3N_4 and SiO_2 and contains only silicon, nitrogen and hydrogen. High-purity Si_3N_4 without sintering aids can be obtained by pyrolyzing PHPS.

The studies of crystallization of amorphous silicon nitride have been reported by some working groups.⁴⁻⁶⁾ Yamada et al.⁴⁾ synthesized amorphous silicon nitride with thermal decomposition of $\text{Si}(\text{NH})_2$. Hojo et al.⁵⁾ synthesized amorphous silicon nitride with thermal decomposition of vapor reaction method. Schmidt et al.⁶⁾ reported the preparation and crystallization of crystalline silicon nitride by pyrolysis of organometallic precursor in NH_3 .

In this paper, we present crystallization behavior of high purity amorphous silicon nitride fiber obtained from PHPS. We also discuss crystallization mechanism and activation energy.

2. Experimental

2.1 Preparation

PHPS that is a precursor of silicon nitride was synthesized by reacting dichlorosilane with NH_3 in pyridine at 0°C. PHPS's simplified structure was given by

This polysilazane is a transparent liquid with low viscosity, composed of silicon, nitrogen and hydrogen. It was heated in pyridine with NH_3 at 80°C to obtain solid polymer that is soluble in pyridine, xylene, etc. PHPS fiber was continuously prepared by dry spinning. The PHPS fiber was pyrolyzed at 600°C for 1h in NH_3 and subsequently annealed at 1300°C for 1h in N_2 . We obtained Si_3N_4 fiber, which shows no peak in the X-ray diffraction measurement and no lattice image in the high-resolational transmission

Fig. 1. SEM photograph of fresh Si_3N_4 fiber.Table 1. An Elemental Analysis of the Amorphous PHPS-Derived Si_3N_4 Fiber

sample	Composition (wt%)				Si/N
	Si	N	O	C	
Amorphous Si_3N_4 fiber*	58.3	37.4	3.58	0.7	0.78

*The fiber was obtained by N_2 -annealing at 1300°C for 1 h after pyrolyzing at 600°C in NH_3 for 1 h.

electron micrograph (TEM). These results indicate that the structure of Si_3N_4 fiber is amorphous. Figure 1 shows scanning electron microscopy (SEM) of the Si_3N_4 fiber.

Table 1 shows elemental analysis result of this amorphous Si_3N_4 fiber. The Si/N atomic ratio is 0.78, which is close to stoichiometric Si_3N_4 . We assume that surplus Si is caused by SiO_x or dangling bond.

2.2 Heat treatment

Fiber was placed (1) on a carbon boat, or (2) in-bedded in BN powder. The fiber was heated in a programmable electric furnace at 1400, 1425, 1450, 1475 and 1500°C for 1–100h in N_2 flow. Heating rate was 10°C per min.

2.3 Characterization

X-ray diffraction (XRD) measurements were performed on heat-treated fiber with Cu $K\alpha$ radiation using an automated powder diffractometer with a monochromator.* Yamada et al.⁷⁾ reported amorphous fraction estimated from the amount of evolved NH_3 in the hydrolysis of partially crystallized Si_3N_4 was in good agreement with that determined by XRD measurement. We determined degree of crystallinity from integrated intensity of (101), (201), (102) and (210) peaks of α - Si_3N_4 .

Transmission electron microscopy (TEM), selected area electron diffraction were used for crystal phase detection, and the morphology of the fiber was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1 Heat treatment without BN powder

Prochazka and Greskovich⁸⁾ reported the crystalli-

zation of amorphous Si_3N_4 powder synthesized from SiH_4 - NH_3 began over 1480°C in N_2 . Futaki et al.⁹⁾ also reported the crystallization temperature of amorphous Si_3N_4 powder synthesized from SiCl_4 - H_2 - NH_3 in a hybrid plasma was as high as 1500°C in N_2 , and Hojo et al.⁵⁾ also reported the crystallization temperature of amorphous Si_3N_4 powder synthesized from $\text{Si}(\text{CH}_3)_4$ - NH_3 occurred between 1500 and 1550°C in N_2 . In these cases crystal phase was only α - Si_3N_4 .

Figure 2(a) shows time dependence of crystallinity of amorphous Si_3N_4 fiber that was heated at 1400, 1450 and 1500°C . The crystallinity of the amorphous

(a)

(b)

Fig. 2. (a) Time dependence of crystallinity of amorphous Si_3N_4 fiber that was heated at 1400, 1450 and 1500°C : heat treatment without BN powder, (b) Time dependence of crystallinity of amorphous Si_3N_4 fiber that was heated at 1400, 1450 and 1500°C : heat treatment with BN powder.

Fig. 3. X-ray diffraction pattern of heat-treated amorphous Si_3N_4 fiber at $1500^\circ\text{C} \times 5\text{h}$.

* Model RINT, Rigaku Denki Co., Ltd.

Fig. 4. SEM photographs of heat-treated Si_3N_4 fiber without BN powder. (a) Heat treatment at $1400^\circ\text{C} \times 25\text{h}$, (b) Heat treatment at $1400^\circ\text{C} \times 100\text{h}$, (c) Fracture surface of heat-treated fiber at $1400^\circ\text{C} \times 25\text{h}$.

Si_3N_4 fiber at 1400°C for 100h is 0.7. The crystallinity is already 0.6 for heat-treated fiber at 1500°C for 5h. This tendency is consistent with the Refs.^{5),8),9)}

Figure 3 shows typical X-ray diffraction patterns. Crystal phase is only $\alpha\text{-Si}_3\text{N}_4$. It is known that $\alpha \rightarrow \beta$ phase transformation proceeds via liquid phase.¹⁰⁾ This suggests that liquid phase does not produce in Si_3N_4 fiber.

From the elemental analysis of the amorphous Si_3N_4 fiber (Table 1), a small amount of impurities such as carbon and oxygen exist in the fiber. We assume that carbon is caused by xylene which is the solution of the spinning dope. SiC and carbon phases are not found from various measurements. This carbon seems to exist as free carbon. Oxygen is presumably originated from the adventitious water incorporated into the fiber during manufacturing steps such as spinning and pyrolysis.

SEM and TEM photographs of the heat-treated fiber at 1400°C are shown in Figs. 4(a)–(c) and Fig. 5. Whisker was not found in these fibers. The particle size seems to increase with increasing crystallinity. The size of the particles on the fiber, which have 0.7 crystallinity, did not change for further calcination. The maximum size of the particle is about $20\text{ }\mu\text{m}$. TEM photograph shows crystalline particles

$\times 3,000,000$

Fig. 5. TEM photograph of heat treatment at $1400^\circ\text{C} \times 100\text{h}$ without BN powder.

are all $\alpha\text{-Si}_3\text{N}_4$. By Fig. 4(c), the crystalline particles seem to grow on the surface of the fiber, and they are not found inside of the fiber. This suggests that crystallization proceeds by vapor phase growth mechanism.

The kinetic data, shown in Fig. 2, could be represented by first order kinetic equation defined as follows.⁴⁾

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (1)$$

where k is a reaction rate constant, α is the weight fraction of crystalline Si_3N_4 in the samples and t is the isothermal ageing time. The temperature dependence of the rate constant k is given by the Arrhenius equation :

$$k = Ae^{-E/RT} \quad (2)$$

where A is a frequency factor, E the activation energy for crystallization, R the gas constant and T the absolute temperature.

Figure 6(a) shows Arrhenius plot of the rate constant against temperature in the crystallization of amorphous Si_3N_4 fiber. This one was obtained from Fig. 2(a). From this, an activation energy of 602 kJ/mol was calculated. This value is smaller than that of 890 kJ/mol reported by Yamada et al.,⁴⁾ but larger than that of 306 kJ/mol reported by Riedel.¹¹⁾ The difference of the value is due to the purity of samples, the sample of Yamada et al. is high purity but the sample of Riedel contains 5.3 wt% oxygen and 0.8 wt% chlorine.

Rate constant of crystallinities of Si_3N_4 fiber was considerably small, compared with that of other powder samples. This experimental result may be understood by taking account of the specific surface area. The value of the surface area of our smooth columnar fiber is calculated $1.7\text{ m}^2/\text{g}$ from diameter of $10.0\text{ }\mu\text{m}$ and density of 2.4 g/cm^3 . The specific surface areas of reported Si_3N_4 powder samples, other polymeric precursors using plasma ($60\text{--}70\text{ m}^2/\text{g}$) for pyrolysis⁹⁾ are larger than our fiber.

According to our experimental results, crystallization of amorphous Si_3N_4 fiber without BN powder proceeds by vapor phase growth mechanism. It has been discussed that thin SiO_2 layer exists on surface

(a)

(b)

Fig. 6. (a) Arrhenius plot of the rate constant in the crystallization of amorphous Si_3N_4 fiber: heat treatment without BN powder, (b) Arrhenius plot of the rate constant in the crystallization of amorphous Si_3N_4 fiber: heat treatment with BN powder.

of Si_3N_4 and that SiO gas occurs from SiO_2 in low oxygen partial pressures. Reaction of vapor SiO with N_2 ⁵⁾ may nucleate crystalline Si_3N_4 .

3.2 Heat treatment with BN powder

Time dependence of crystallinity of amorphous Si_3N_4 fiber, which was heat-treated in BN powder at 1400, 1450 and 1500°C for 1h, is shown in Fig. 2(b). Comparing to heat-treating without BN powder, it is clear that crystallization is particularly retarded at 1400 and 1450°C. The crystallinity for heat treatment at 1400°C for 100h was about 0.01. But the crystallinity became 0.35 when the fiber was heat-treated in BN powder at 1500°C for 5h. Only $\alpha\text{-Si}_3\text{N}_4$ was observed by XRD measurement.

Figure 7 shows SEM photographs of heat-treated fiber at 1400°C in BN powder. Crystalline particles can not be observed by SEM. These experimental results indicate that BN powder suppresses the crystallization and crystal growth. Hojo et al.⁵⁾ reported that BN powder suppressed evolution of SiO gas. BN powder suppresses crystallization of amorphous Si_3N_4 through vapor phase.

According to these experimental results, in the case of heat treatment in BN powder, we assume that crystallization proceeds by solid phase growth

Fig. 7. SEM photographs of heat-treated Si_3N_4 fiber with BN powder. (a) Heat treatment at 1400°C $\times$ 25h, (b) Heat treatment at 1400°C $\times$ 100h.

Fig. 8. Relation between heat-treated time and temperature when the crystallinity α is assumed 0.01.

mechanism.

Arrhenius plot of the rate constant against temperature in the crystallization of amorphous Si_3N_4 fiber in BN powder is shown in Fig. 6(b). An activation energy of 1273 kJ/mol was considered. This value is about twice larger than the value of 602 kJ/mol which was calculated from heat-treated fiber without BN powder. 1273 kJ/mol is thought to be the intrinsic activation energy of crystallization of Si_3N_4 fiber.

In ceramic matrix composite, ceramic fiber is surrounded with dense matrix. Crystallization of amorphous ceramic fiber via vapor phase may be inhibited. Durability of Si_3N_4 fiber, incorporated into ceramic matrix, at high temperature can be estimated by using the activation energy of 1273 kJ/mol.

From Eqs. (1) and (2), t is represented as follows.

$$t = -\frac{\ln(1-\alpha)}{A} e^{-E/RT} \quad (3)$$

Figure 8 shows temperature dependence of t when value of α is assumed 0.01, which is allowed for practical use such as fiber reinforced composites.¹²⁾ A value of t at 1300 and 1400°C shows about 5×10^4 h and 6×10 h, respectively.

4. Summary

The crystallization of high purity amorphous polymer-derived Si_3N_4 fiber, which was heat-treated with and without BN powders, was investigated. In the case without BN powder, the crystallization proceeds by vapor phase growth mechanism through

SiO gas. The activation energy of 602 kJ/mol was calculated. In the case with BN powder, the crystalline growth and crystallization through vapor phase was fairly suppressed. The crystallization proceeds by solid phase growth mechanism. The activation energy of 1273 kJ/mol was calculated.

Durability of Si_3N_4 fiber in a ceramic matrix composite was estimated. Si_3N_4 fiber may remain amorphous at 1300°C for 5×10^4 h and at 1400°C for 6×10 h, respectively.

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