

An Improved Procedure for Fabricating SiO₂-TiO₂-Phenolic Resin Hybrid Fibers as Precursors for Long Si-Ti-C Fibers by Sol-Gel Processing

Isao Hasegawa,^{a*} Yuka Fukuda^a & Meisetsu Kajiwara^b

^aDepartment of Applied Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu-City, Gifu 501-11, Japan

^bDepartment of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-Cho, Chikusa-Ku, Nagoya-City, Aichi 464-01, Japan

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Abstract

Synthesis conditions for producing SiO₂-TiO₂-phenolic resin hybrid fibers with a wide range of Si-to-Ti atomic ratios from tetraethoxysilane, titanium tetrakis(2,4-pentanedionate) and novolak-type phenolic resins by sol-gel processing have been investigated. It was found that 2,4-pentanedione was an effective solvent for the sol-gel reaction in order to produce the hybrid fibers. For favorable spinnability of the hybrid fibers from the solutions it was necessary to adjust critically the amounts of H₂O and of acid, which were added to promote hydrolysis and polycondensation of the Si and Ti compounds in the solutions, according to their Si-to-Ti ratios. The amounts found to be optimal for spinning the hybrid fibers were in proportion to the Si-to-Ti ratio of the solutions. Using these combinations, SiO₂-TiO₂-phenolic resin hybrid fibers with various Si-to-Ti ratios could then be produced, which could then be converted into Si-Ti-C fibers by carbothermal reduction at 1500°C in Ar. © 1997 Elsevier Science Limited.

1 Introduction

Silicon-based non-oxide ceramics, such as silicon carbide (SiC) and silicon nitride (Si₃N₄) are important in fiber form as reinforcing components for various composites because of their high strength and thermal stability. Numerous studies have been made of their synthesis and applications.¹

On the basis of pioneering work by Yajima *et al.*,² polycarbosilanes have been used as precursors for the commercial fabrication of continuous SiC fibers, which have been named Nicalon fibers. Introduction of another metal such as Ti into the polymers has been possible, which gives Si-Ti-C-O (Tyranno) fibers with enhanced stability upon pyrolysis.^{3,4}

Sol-gel processing combined with carbothermal reduction has also been shown to be suitable for producing continuous SiC⁵⁻⁷ and Si₃N₄⁸ fibers. Tetraethoxysilane [Si(OC₂H₅)₄, TEOS] and phenolic resins undergo a sol-gel reaction in acidic ethanolic solutions to give hybrid fibers consisting of silica (SiO₂) and phenolic resin components. Without any pretreatment, carbothermal reduction of the hybrid fibers at 1500°C under Ar or N₂ atmosphere leads to the formation of continuous SiC or Si₃N₄ fibers, respectively. On the basis of this procedure, Si-Ti-C fibers can be synthesized from SiO₂-titania (TiO₂)-phenolic resin hybrid fibers which are prepared by adding titanium tetrakis(2,4-pentanedionate) [Ti(C₅H₇O₂)₄, TTP] as a Ti source into the starting solutions.⁹

In a previous study on the synthesis of Si-Ti-C fibers,⁹ however, only fibers with Si-to-Ti atomic (Si/Ti) ratios down to 9.9 could be obtained. In other words, fibers with higher Ti contents could not be fabricated from the TEOS-TTP-phenolic resin-ethanol-H₂O-HCl system. This was attributed to the formation of precipitates on preparing starting solutions with higher Ti compositions.

Consequently, the aim of this study has been to prepare Si-Ti-C fibers with a wide range of Si/Ti

*To whom correspondence should be addressed.

ratios by sol-gel processing combined with carbothermal reduction. This paper reports synthesis conditions for preparing single-phase starting solutions with various Si/Ti ratios to give SiO₂-TiO₂-phenolic resin hybrid fibers and fibrous products after heat-treatment at 1500°C in Ar.

2 Experimental procedure

2.1 Materials

TEOS (Nacalai Tesque, Inc.) and a 65 wt% 2-propanol solution of TTP (Matsumoto Seiyaku Co.) were used as a Si and a Ti source, respectively. Novolak-type phenolic resins (PSM-2317, Gun-ei Kagaku Kogyo Co.)⁵ were used as the organic component of the precursor fibers. Hydrochloric acid (aqueous HCl solutions) and sulfuric acid (H₂SO₄) were used as catalysts for the hydrolysis and polycondensation of TEOS and TTP. 2-methoxyethanol and 2,4-pentanedione were applied to test their merits as solvents.

2.2 Preparation of starting solutions

Starting solutions containing HCl as catalyst and 2-methoxyethanol or 2,4-pentanedione as solvent were prepared in the same manner as has been described.⁹

Starting solutions prepared using H₂SO₄ and 2,4-pentanedione were prepared as follows. The phenolic resins were dissolved in 5.0 ml of 2,4-pentanedione to which TEOS, the 2-propanol solution of TTP, H₂SO₄, and H₂O were added, whereby the total amount of TEOS and TTP in the mixture was fixed at 1.68×10^{-2} mole.

The atomic ratio of C to the total amount of Si and Ti in the phenolic resins, designated as C*/(Si + Ti), was fixed at 4.0 in order to determine the optimal amounts of H₂O and H₂SO₄ for the spinning of fibers from the starting solutions with different Si/Ti ratios. Amounts of H₂O and H₂SO₄ are designated in terms of the H₂O/(Si + Ti) and H₂SO₄/(Si + Ti) ratios, respectively, i.e., the molar ratios to the total amount of Si and Ti in the solutions. Solutions with different C*/(Si + Ti) ratios but with a fixed Si/Ti ratio of 1.0 were also prepared.

These solutions were stirred for 20–40 min at room temperature and then held at 65°C. The volume of the solutions decreased and their viscosities increased with time, resulting in viscous sols. They were then held at room temperature to spin fibers. This is because gelation of the sols took place in *ca.* 5 min if the sols were kept held at 65°C. Fibers were drawn from the viscous sols by dipping glass rods into the solutions and by then withdrawing them.

The fibers as synthesized were sticky, which is attributable to the inclusion of solvent. In order to avoid coalescence of the fibers, they were dried at room temperature at least overnight.

2.3 Carbothermal reduction of the precursor fibers

The dried fibers were placed on alumina boats without further pre-treatment and fired at 1500°C for 4 h in flowing argon (100 cm³ min⁻¹) in a tube furnace. Heat-treatment at 1500°C is necessary for complete conversion of the SiO₂-TiO₂-phenolic resin hybrid fibers to Si-Ti-C fibers.⁹ The heating rate was *ca.* 10°C min⁻¹.

2.4 Analytical procedures

Fibers prepared by the sol-gel reaction were characterized with a Perkin-Elmer FT-IR 1640 spectrometer. The C*/(Si + Ti) ratio of the fibers was estimated from their TG curves obtained with a Shimadzu TGA-50H. The procedure for the determination was described in a previous paper.⁹ The Si/Ti ratios of the fibers obtained by the sol-gel reaction and of those formed by the heat-treatment were determined by EDX analysis using a Horiba EMAX-2770 combined with a TOPCON ABT-60 scanning electron microscope. The conditions for the analyses were the same as those previously detailed.⁹

The XRD patterns of powdered samples of the fibrous products obtained by the heat-treatment at 1500°C were recorded on a Rigaku RAD III-A diffractometer using Cu K α radiation.

3 Results and discussion

3.1 Effect of solvent type on the preparation of single-phase starting solutions

When ethanol was used as solvent for the reaction to produce SiO₂-TiO₂-phenolic resin hybrid fibers in the previous study,⁹ only solutions with Si/Ti ratios down to 10.0 could be prepared. Ethanol solutions with Si/Ti ratios lower than 10.0 gave precipitates immediately after the preparation, which were found to consist of phenolic resin and TiO₂ components.

By contrast, when 2-methoxyethanol was used as solvent, single-phase solutions with Si/Ti ratios down to 5.0 could be prepared. These solutions gave fibers after holding at 65°C. The fibers can be characterized as SiO₂-TiO₂-phenolic resin hybrid fibers, since the fibers gave rise to bands due to the SiO₂, TiO₂, and phenolic resin components in their FT-IR spectra. (Identification of the hybrid fibers with FT-IR spectroscopy has already been described.⁹ All the hybrid fibers prepared in this study were characterized in this manner.) The 2-

methoxyethanol is therefore more effective than ethanol as solvent for the sol-gel reaction. Solutions with Si/Ti ratios lower than 5.0, however, did yield precipitates even if 2-methoxyethanol was used as solvent.

These findings imply that the exchange reaction between the ligand of TTP and the solvent takes place immediately and that the stability of newly coordinated ligands is an important factor for preparing single-phase solutions consisting of TEOS, TTP, and the phenolic resins.

Accordingly, 2,4-pentanedione, which corresponds to the ligand of TTP, was selected as solvent for the sol-gel reaction. With the aid of this solvent, single-phase starting solutions with various Si/Ti ratios could be prepared, from which SiO₂-TiO₂-phenolic resin hybrid fibers could be spun.

3.2 Effect of the amount of H₂O and H₂SO₄ on the spinnability of SiO₂-TiO₂-phenolic resin hybrid fibers

Table 1 shows spinnability and dimensions of SiO₂-TiO₂-phenolic resin hybrid fibers derived from TEOS-TTP-phenolic resin-H₂O-HCl-2,4-pentanedione solutions with a Si/Ti ratio of (a) 3.0 and (b) 5.0, a HCl/(Si + Ti) ratio of 0.10, and a C*/(Si + Ti) ratio of 4.0 as a function of the H₂O/(Si + Ti) ratio. The spinnability of the fibers shows an optimum when the H₂O/(Si + Ti) ratio is 1.04–1.37 notwithstanding any difference in the Si/Ti ratio of the solutions. When the ratio is 2.03, however, the fibers can be drawn from the solution with a Si/Ti ratio of 5.0 but not from that with a Si/Ti ratio of 3.0. This would suggest that the amount of water added to the starting solutions has to be controlled according to the Si/Ti ratio for optimal spinnability of the hybrid fibers. Moreover, the amount of water should be reduced with decreasing Si/Ti ratio of the solutions.

Because of the limit to solubility of HCl in water, there is a lower bound to the H₂O/(Si + Ti) ratios which can be achieved in the starting solutions using hydrochloric acid. Accordingly, H₂SO₄ was used instead of HCl as catalyst for further investigation of the spinnability of the hybrid fibers. For this purpose, we prepared TEOS-TTP-phenolic resin-H₂SO₄-H₂O-2,4-pentanedione solutions with Si/Ti ratios of 0, 1.0, 3.0, and 5.0, whose H₂SO₄/(Si + Ti) ratios were kept constant at 0.1, 0.1, 0.2, and 0.4, respectively, the C*/(Si + Ti) ratios being all fixed at 4.0.

Figures 1 and 2 show the effect on spinnability of the amounts of H₂O and of H₂SO₄ in the starting solutions, respectively. Spinnability was assessed using the length and diameter of the fibers obtained. It is apparent from Figs 1 and 2 that for each different Si/Ti ratio in the solutions there are ranges of H₂O/(Si + Ti) and H₂SO₄/(Si + Ti) ratios suitable for spinning fibers.

It should be noted that the solution with a Si/Ti ratio of 0 gave TiO₂-phenolic resin hybrid fibers, which do not contain the SiO₂ component. A variety of TiO₂-organic hybrid fibers have so far been prepared using various organic compounds,^{10–13} which can be used as precursors of TiO₂ or TiC fibers. In addition to these, the novolak-type phenolic resins are found to be usable as another organic source of the TiO₂-organic hybrid fibers when critical amounts of H₂O and H₂SO₄ are added to the starting solution.

Hybrid fibers could be spun from solutions with the H₂O/(Si + Ti) ratios indicated by closed and open circles in Fig. 1. When excess H₂O was added, the solutions gave gels without spinnability, although their viscosity increased with holding time at 65°C. On the other hand, where the amount of added H₂O was too small, the viscosity of the solutions hardly increased, resulting in bulk precipitates.

Table 1. Spinnability and dimensions of SiO₂-TiO₂-phenolic resin hybrid fibers prepared from TEOS-TTP-H₂O-HCl-2,4-pentanedione solutions with a HCl/(Si + Ti) ratio of 0.10 and a C*/(Si + Ti) ratio of 4.0

(a) Si/Ti ratio = 3.0

H ₂ O/(Si + Ti) ratio	Spinnability	Length cm ⁻¹	Diameter μm ⁻¹
0.71	no	—	—
1.04	yes	≥50	11–168
1.37	yes	≥50	26–159
1.70	yes	≥50	129–189
2.03	no	—	—

(b) Si/Ti ratio = 5.0

H ₂ O/(Si + Ti) ratio	Spinnability	Length cm ⁻¹	Diameter μm ⁻¹
0.71	no	—	—
1.04	yes	≥50	5–125
1.37	yes	≥50	5–130
1.70	yes	≥50	8–132
2.03	yes	5–10	40–270
2.36	no	—	—

In addition, even if the solutions showed spinnability, the types of hybrid fiber obtained were different depending on their $H_2O/(Si+Ti)$ ratios. When the amount of H_2O was small in the spinnable range of $H_2O/(Si+Ti)$ ratios, the fibers obtained were thin ($5\text{--}20\ \mu\text{m}$ in diameter) and short (*ca.* $20\text{--}30\ \text{cm}$ in length). When the amount of H_2O was large, the resulting fibers were thick ($50\text{--}100\ \mu\text{m}$ in diameter) and short (*ca.* $20\text{--}30\ \text{cm}$ in length). However, when the amount of H_2O was optimal (closed circles in Fig. 1) hybrid fibers $10\text{--}50\ \mu\text{m}$ in diameter and over $50\ \text{cm}$ in length could be obtained. Figure 3 shows a bundle of the SiO_2 - TiO_2 -phenolic resin hybrid fibers prepared from a solution with a Si/Ti ratio of 1.0.

The spinnability also differs with the amount of H_2SO_4 added to the solutions. When the amount was large, the fibers could be drawn but were broken into small pieces on drying. Granular precipitates were formed from the solutions when their $H_2SO_4/(Si+Ti)$ and Si/Ti ratios were both high. On the other hand, when the $H_2SO_4/(Si+Ti)$ ratio was low, the solutions gave white precipitates. On the basis of these facts, optimal $H_2SO_4/(Si+Ti)$ ratios for spinning the fibers from the solutions at each Si/Ti ratio can be plotted (closed circles) as in Fig. 2.

It should be noted that the optimal $H_2O/(Si+Ti)$ and $H_2SO_4/(Si+Ti)$ ratios for spinning the hybrid fibers from the solutions at each Si/Ti ratio have small ranges centering at the ratios which are shown (closed circles) in Figs. 1 and 2, respectively. The small spinnability range of the $H_2O/(Si+Ti)$ ratios has been demonstrated with regard to the system containing HCl as catalyst (see Table 1).

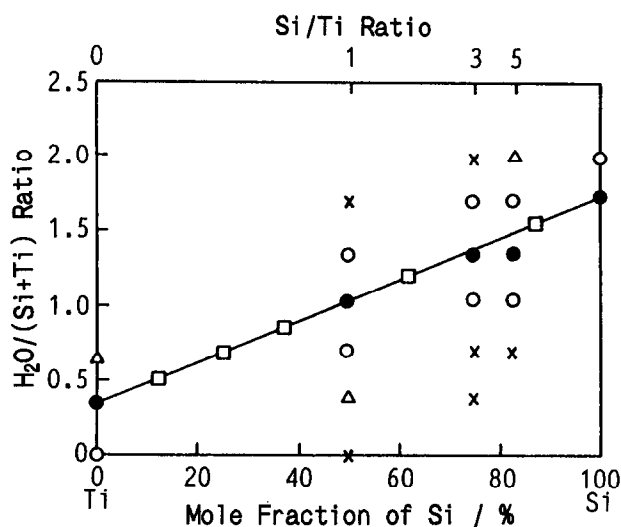


Fig. 1. The effect of $H_2O/(Si+Ti)$ ratio of the starting solutions on spinnability of SiO_2 - TiO_2 -phenolic resin hybrid fibers from the solutions with various Si and Ti compositions. ●: optimal for spinning, ○: possible to spin, △: difficult to spin, ×: impossible to spin, □: values of $H_2O/(Si+Ti)$ ratios applied to preparation of the hybrid fibers from the solutions with the Si/Ti ratios, which were estimated from the linear correlation.

For the solutions containing H_2SO_4 as catalyst, the spinnability range of the $H_2O/(Si+Ti)$ ratios is *ca.* ± 0.2 and that of the $H_2SO_4/(Si+Ti)$ ratios is *ca.* ± 0.02 at each Si/Ti ratio.

Concerning the $H_2O/(Si+Ti)$ and $H_2SO_4/(Si+Ti)$ ratios optimal for drawing hybrid fibers from the solutions at each Si/Ti ratio, it is noteworthy that these ratios are directly proportional to the Si/Ti ratio (in mole fractions), as is shown in Figs. 1 and 2, respectively. Accordingly, the amounts of H_2O and H_2SO_4 for preparing starting solutions with Si/Ti ratios of 1/7, 1/3, 3/5, 5/3, and 7.0 were decided on the basis of the proportionality shown as open squares in Figs. 1 and 2, respectively. Hybrid fibers could then be fabricated from solutions with these compositions.

In addition, the H_2O/Si and H_2SO_4/Si ratios optimal for spinning SiO_2 -phenolic resin hybrid

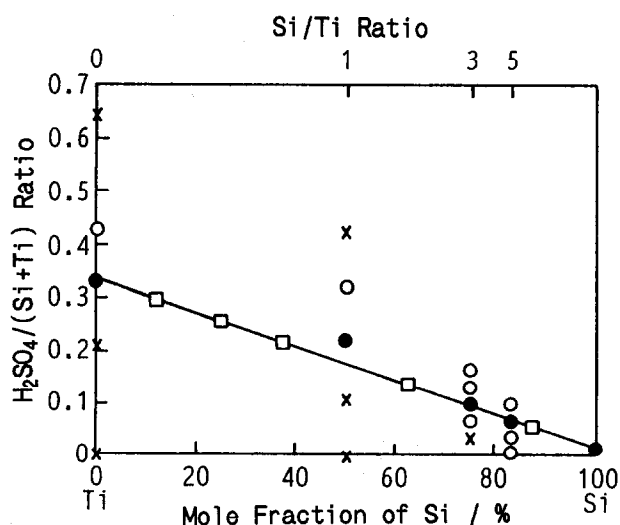


Fig. 2. The effect of $H_2SO_4/(Si+Ti)$ ratio of the starting solutions on spinnability of SiO_2 - TiO_2 -phenolic resin hybrid fibers from the solutions with various Si and Ti compositions. ●: optimal for spinning, ○: possible to spin, ×: impossible to spin, □: values of $H_2SO_4/(Si+Ti)$ ratios applied to preparation of the hybrid fibers from the solutions with the Si/Ti ratios, which were estimated from the linear correlation.

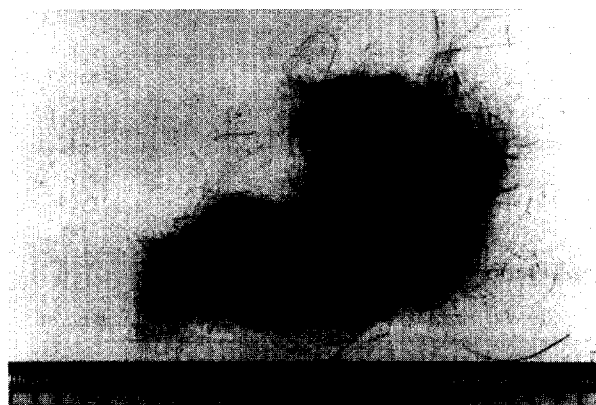


Fig. 3. A photograph of a bundle of SiO_2 - TiO_2 -phenolic resin hybrid fibers prepared from the starting solution with a Si/Ti ratio of 1.0; an $H_2O/(Si+Ti)$ ratio of 1.0; an $H_2SO_4/(Si+Ti)$ ratio of 0.2, and a $C^*/(Si+Ti)$ ratio of 4.0.

fibers from TEOS-phenolic resins-H₂O-H₂SO₄-2, 4-pentanedione solutions were also found to follow a direct proportionality. This fact would suggest that the relation between the H₂O/(Si + Ti) ratio and the Si/Ti ratio may be estimated just by determining the H₂O/Si ratio suitable for spinning SiO₂-phenolic resin hybrid fibers, and the H₂O/Ti ratio suitable for spinning TiO₂-phenolic resin hybrid fibers. Similarly, the relation between the H₂SO₄/(Si + Ti) ratio and the Si/Ti ratio may be estimated from the H₂SO₄/Si and H₂SO₄/Ti ratios.

The holding time at 65°C of the solutions used for spinning the hybrid fibers is shown in Table 2. With increasing Si/Ti ratio, longer soaking times are necessary. This is due to the fact that the volumes of the starting solutions are larger when their Si/Ti ratio decreases. Since a 65 wt% 2-propanol solution of TTP is used as the Ti-source, the total volume of the starting solution becomes larger when the Ti content is higher. Therefore, it takes more time to evaporate the solvent and the low boiling components from the solutions which have lower Si/Ti ratios in order to reach the desired viscosities.

3.3 Carbothermal reduction of the precursor fibers

When the hybrid fibers were heated at 1500°C for 4h in Ar, fibrous products were obtained, whose XRD patterns are shown in Fig. 4. The β-SiC and/or TiC phases give rise to peaks in the patterns, meaning that the hybrid fibers can be converted into carbide fibers by the heat-treatment. Figure 5 shows a SEM photograph of a Si-Ti-C fiber prepared from the starting solution with a Si/Ti ratio of 1.0. The Si/Ti ratio of Si-Ti-C fibers obtained is shown in Table 2, indicating that carbide fibers with a variety of Si/Ti ratios can be synthesized by this procedure. In addition, TiO₂-phenolic resin hybrid fibers are found to give TiC fibers as a result of the heat-treatment [Fig. 4(a)]. The ceramic yield of the carbide fibers is *ca.* 32% on average (Table 2).

The C*/(Si + Ti) ratio of the hybrid fibers can be changed just by varying the amount of the phenolic resins dissolved in the starting solutions. Despite the difference in the amounts of the resins, hybrid fibers with variable carbon contents and Si/Ti ratios can be prepared by applying the relations between the H₂O/(Si + Ti) and H₂SO₄/(Si + Ti) ratios and the Si/Ti ratio as is shown in Figs. 1 and 2, respectively.

Table 3 shows the relation between the C*/(Si + Ti) ratio of the starting solutions with a Si/Ti ratio of 1.0; a H₂O/(Si + Ti) ratio of 1.0; an H₂SO₄/(Si + Ti) ratio of 0.2, and that of SiO₂-TiO₂-phenolic resin hybrid fibers prepared from the solutions. The ratio of the starting solutions is not consistent with that of the hybrid fibers derived from them. However, these ratios vary in a consistent way, indicating that the carbon content in the hybrid fibers is

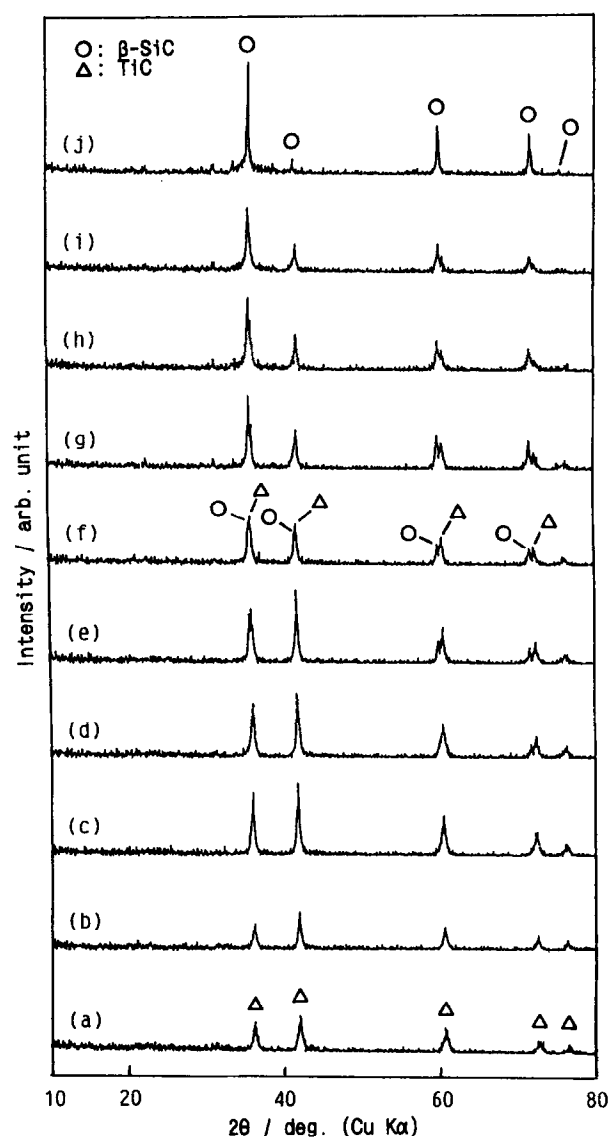


Fig. 4. XRD patterns of fibrous products obtained by carbothermal reduction at 1500°C in Ar for 4 h of (a) TiO₂-phenolic resin hybrid fibers, SiO₂-TiO₂-phenolic resin hybrid fibers formed from the starting solutions with a Si/Ti ratio of (b) 1/7, (c) 1/3, (d) 3/5, (e) 1.0, (f) 5/3, (g) 3.0, (h) 5.0, (i) 7.0, and (j) SiO₂-phenolic resin hybrid fibers. The C*/(Si + Ti) ratio of the starting solutions were kept constant at 4.0.

Table 2. The holding time of the starting solutions with various Si and Ti compositions at 65°C for fabricating the hybrid fibers and the Si/Ti ratio and ceramic yield of fibrous products formed by heat-treatment of the hybrid fibers at 1500°C in Ar for 4 h. The C*/(Si + Ti) ratio of the starting solutions was kept constant at 4.0

Si/Ti ratio of the starting solution	Si only	7.0	3.0	5/3	1.0	3/5	1/3	1/7	Ti only
Soaking time at 65°C h ⁻¹	3.5	4.5	4.5	4.5	6.0	8.3	9.0	9.0	9.0
Si/Ti ratio of carbide fibers obtained from precursor fibers	Si only	5.13	3.93	2.02	1.15	0.67	0.30	0.08	Ti only
Ceramic yield %		28.1	32.0	31.7	29.5	31.5	33.4	34.8	33.9

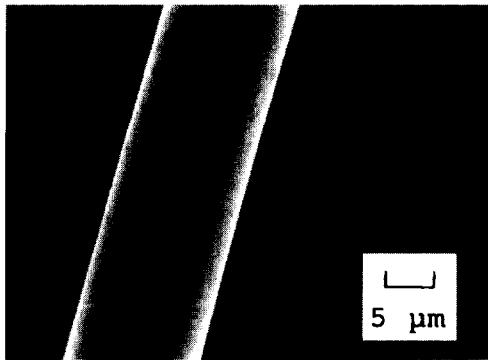


Fig. 5. A SEM photograph of a Si-Ti-C fiber with a Si/Ti ratio of 1.15.

adjustable with the amount of the phenolic resins used for preparing the solutions.

Hybrid fibers with a Si/Ti ratio of 1.0 and $C^*/(Si + Ti)$ ratios of 1.0–5.0 could also be converted into Si-Ti-C fibers upon firing at 1500°C for 4 h in Ar, as shown in Fig. 6. The ceramic yield of the fibers is shown in Table 3.

In Fig. 6(a), the peaks (except for the β -SiC phases) appear at higher angles than can be assigned to TiC. This suggests the formation of carbon-deficient titanium carbide, TiC_{1-x} , in the fibrous products synthesized from the starting solution with a $C^*/(Si + Ti)$ ratio of 1.0, since such peak shifts are related to carbon deficiency in the TiC phase.¹⁴ On the basis of the relationship between the cubic lattice parameter, a_0 , and the amount of deficient carbon, x , of TiC_{1-x} ,¹⁴ a

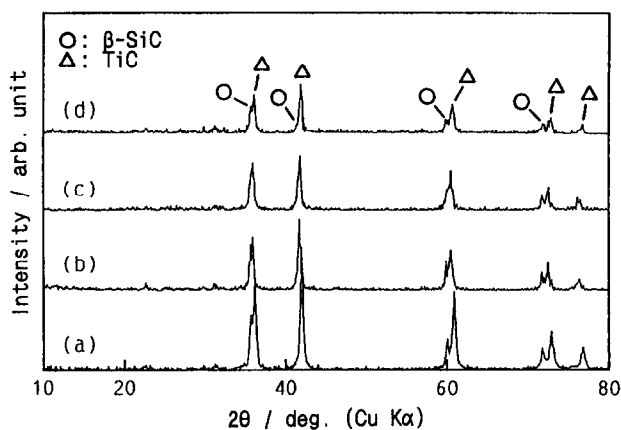


Fig. 6. XRD patterns of fibrous products yielded by carbothermal reduction at 1500°C in Ar for 4 h of SiO_2 - TiO_2 -phenolic resin hybrid fibers prepared from the starting solutions with a Si/Ti ratio of 1.0; a $H_2O/(Si + Ti)$ ratio of 1.0; an $H_2SO_4/(Si + Ti)$ ratio of 0.2, and a $C^*/(Si + Ti)$ ratio of (a) 1.0, (b) 2.0, (c) 3.0, and (d) 5.0.

Table 3. $C^*/(Si + Ti)$ ratios of the starting solutions (Si/Ti ratio=1.0, $H_2O/(Si + Ti)$ ratio=1.0, $H_2SO_4/(Si + Ti)$ ratio=0.2) and SiO_2 - TiO_2 -phenolic resin hybrid fibers prepared from the solutions, and ceramic yields of Si-Ti-C fibers formed from the hybrid fibers

$C^*/(Si + Ti)$ ratio of the starting solution	1.0	2.0	3.0	4.0	5.0
$C^*/(Si + Ti)$ ratio of the precursor fibers	1.3	2.2	3.2	4.3	5.4
Ceramic yield %	28.9	30.0	33.0	31.5	36.3

composition of $TiC_{0.5}$ is indicated for the fibrous products ($a_0 = 0.4299$ nm). The formation of $TiC_{0.5}$ in the products can be ascribed to a low carbon content in the precursor fibers. The formation of TiC_{1-x} , however, can be prevented by adjusting the carbon content in the hybrid fibers, as seen from the XRD patterns shown in Figs. 6(b), (c) and (d).

4 Conclusions

A synthesis process has been established for preparing SiO_2 - TiO_2 -phenolic resin hybrid fibers with a wide range of Si/Ti ratios from TEOS, TTP, and the novolak-type phenolic resins by sol-gel processing. It was found that 2,4-pentanedione acted as an effective solvent for the sol-gel reaction. Depending on the Si/Ti ratio of the solutions, varying amounts of H_2O and H_2SO_4 were required to be added to the solutions to achieve favorable spinnability of the hybrid fibers. It was found that there were linear correlations between the Si/Ti ratio and the amounts of H_2O and H_2SO_4 required for spinnability. On the basis of these relations, hybrid fibers with a variety of Si/Ti ratios could be produced. Heat-treatment of the hybrid fibers at 1500°C in Ar for 4 h converted the hybrid fibers into Si-Ti-C fibers. TiO_2 -phenolic resin hybrid fibers could be synthesized by this procedure as well, which resulted in the production of TiC fibers. The carbon content in the hybrid fibers was found to be adjustable with the amount of phenolic resin added to the starting solutions. Hybrid fibers with a low carbon content yielded fibers composed of SiC and TiC_{1-x} .

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