

Silica Gel–Phenolic Resin Hybrid Fibres: New Precursors for Continuous β -Silicon Carbide Fibres

Isao Hasegawa,^{a*} Toshiyuki Nakamura,^a Seiji Motojima^a and Meisetsu Kajiwara^b

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

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

Silica gel–phenolic resin hybrid fibres have been synthesized by hydrolysis and polycondensation of tetraethoxysilane [Si(OC₂H₅)₄, TEOS] in the presence of phenolic resins in ethanol under acidic conditions. The fibres had C:Si atomic ratios of 2.6–5.4 and could be converted into β -silicon carbide (SiC) fibres by carbothermal reduction at 1500 °C under an argon atmosphere.

SiC fibres provide one of several promising reinforcement materials for various composites. Polycarbosilanes¹ are used as precursors in the commercial fabrication of SiC fibres. The subsequent processes of melt-spinning of polycarbosilanes, curing of the resultant fibre bundles and heat-treatment of the cured fibres under an inert atmosphere results in the production of SiC fibres.

An alternative procedure for preparing SiC (and other non-oxide inorganic fibres)² involves the preparation of TEOS-impregnated organic fibres by soaking organic fibres, which show high recoveries of carbonaceous residue after pyrolysis, e.g. phenolic resins in TEOS. The resulting TEOS-impregnated organic fibres are then soaked in water to hydrolyse and polycondense the TEOS within the fibres, yielding silica-impregnated organic fibres. Carbothermal reduction of these fibres under a non-oxidizing atmosphere yields SiC fibres.

These procedures are effective in synthesizing continuous SiC fibres. However, they involve some troublesome steps such as curing of fibrous polycarbosilanes or hydrolysis and polymerization of TEOS-impregnated continuous organic fibres.

Sol–gel processing is one of many procedures for synthesizing oxide ceramic fibres.³ Gels formed by hydrolysis and polymerization of organotrialkoxysilane⁴ or by co-hydrolysis and copolymerization of organoalkoxysilane and tetraalkoxysilane,⁵ and mixtures of gels formed from alkoxysilane and an additional carbon source⁶ have been reported together with their conversion to SiC powders by carbothermal reduction at elevated temperatures in Ar.

In this study, we have investigated on a novel route for the synthesis of continuous SiC fibres by sol–gel processing.

Silica gel–phenolic resin hybrid fibres were prepared as follows. Beaded phenolic resins (PS-2317,† supplied by Gun- ei Kagaku Kogyo Co., Gumma, Japan) were dissolved in ethanol (10 cm³). TEOS (15 cm³) as the Si source was added to the ethanol solution, followed by the addition of distilled water and hydrochloric acid so that the water:TEOS and HCl:TEOS molar ratios of the solutions were 2.0 and 0.01, respectively. The atomic ratios of C in the phenolic resins to Si in TEOS, represented as C*:Si, of the solutions were varied from 1.0 to 5.0 by changing the amount of the phenolic resins (1.0–5.1 g). The solutions were initially stirred for 5 min at room temperature and then allowed to stand at 65 °C. The viscosity of the solutions increased with time and fibres *ca.*

Table 1 C*:Si ratios of the starting solutions and silica gel–phenolic resin hybrid fibres drawn from the solutions just before gelation

C*:Si	
starting solution	hybrid fibres
1.0	1.7
2.0	2.6
3.0	3.4
4.0	4.3
5.0	5.4

30 cm in average length could be drawn by dipping from the solutions 4–4.5 h after preparation.

Bands due to the silica and phenolic resin components appeared in the FTIR spectra of the resultant fibres.‡ A broad signal appeared around 138 ppm in the solid-state ¹³C NMR spectra of the fibres, which were assigned to C atoms in aromatic rings of the phenolic resins. The broad signal is dominant in the spectrum of the resins alone. In the solid-state ²⁹Si NMR spectra of the fibres, a broad signal occurs around –100 ppm accompanying a shoulder at *ca.* –110 ppm; these are assigned to Si(OSi)₃(O[–]) and Si(OSi)₄ silicate units, respectively. This indicates that hydrolysis and polycondensation of TEOS have taken place in the presence of the phenolic resins to yield silica gel–phenolic resin hybrid fibres.

Table 1 shows the C*:Si ratios of the starting solutions and the resultant hybrid fibres. Although the C*:Si ratio of the solution is not equal to that in the hybrid fibres, the carbon content in the hybrid fibres increases with the amount of phenolic resin used for preparing the solutions.

Hybrid fibres with C*:Si=4.3 were heated at 1450 or 1500 °C for 4 h in Ar at a flow rate of 100 cm³ min^{–1}. The hybrid fibres were placed in an alumina boat and the temperature raised from room temperature to 1450 or 1500 °C in *ca.* 2.5 h (at *ca.* 10 °C min^{–1}). The products obtained were fibrous. The fibres heated at 1450 °C were black, while those at 1500 °C were pale grey.

Fig. 1 shows the XRD patterns of the products. In Fig. 1(a),

† The phenolic resins are a mixture of compounds ranging from the dimer to decamer, [(HO)C₆H₄CH₂]_n–(HO)C₆H₄(CH₂OH) (*n*=1–9). Structural isomers are involved in each *n*-mer.

‡ FTIR spectra of samples in the form of KBr pellets were recorded on a Perkin-Elmer FTIR 1640 spectrometer. In the spectra of silica gel–phenolic resin hybrid fibres at C*:Si=4.3, intense bands appeared at 1078 (Si–O–Si str.), 1165, 1185, 1212 (C–O str.), 1458 (C–H def.), 1508, 1560, 1618 (C=C str. in aromatic rings), 1845, 1870, 1944, 1982 (over and combination tones of C–H out-of-plane def.), 2936, 2975, 3022, 3081 (C–H str. on aromatic rings and in methylene groups) and 3422 (O–H str.) cm^{–1}.

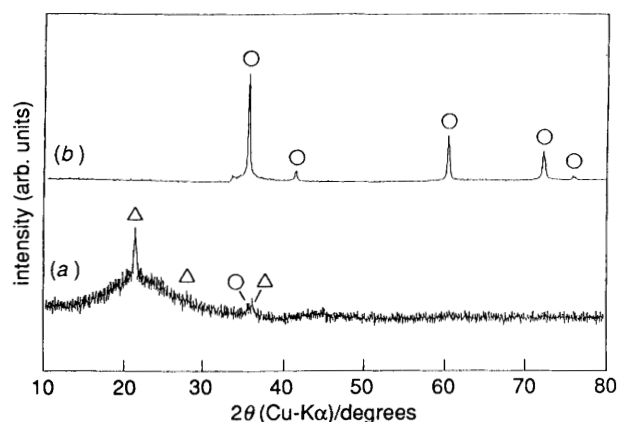


Fig. 1 XRD patterns of products obtained by heating silica gel-phenolic resin hybrid fibres at $C^*:Si = 4.3$ at (a) 1450 and (b) 1500 °C for 4 h in Ar, recorded on a Rigaku RINT 1100 diffractometer using Ni-filtered Cu-K α radiation: (○) β -SiC; (Δ) cristobalite

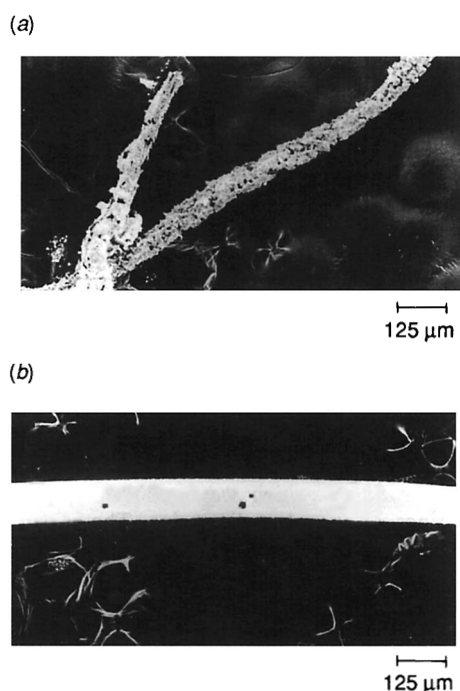


Fig. 2 SEM photographs of SiC fibres produced from the silica gel-phenolic resin hybrid fibres at $C^*:Si = 2.6$ (a) and 4.3 (b), obtained on a TOPCON ABT-60 at an accelerating voltage of 20 kV

peaks at 21.7, 28.2, and 35.9° are assigned to cristobalite, and a small peak at 35.4° to β -SiC. The occurrence of a broad peak centred around 22° indicates the presence of amorphous components, possibly silica and/or carbon. This implies that carbothermal reduction of the hybrid fibres is not complete after heat treatment at 1450 °C for 4 h in Ar.

Intense peaks due to β -SiC are present in the XRD pattern of the fibres heated at 1500 °C for 4 h in Ar [Fig. 1(b)]. No apparent band due to the Si—O stretching is revealed in the range 1000–1100 cm^{-1} of the FTIR spectrum of the fibres, and the most intense band (855 cm^{-1}) is assigned to Si—C stretching. This indicates that carbothermal reduction of the hybrid fibres occurs to give β -SiC fibres under the conditions.

β -SiC fibres can also be synthesized by heating the hybrid fibres with $C^*:Si = 2.6, 3.4$ and 5.4 at 1500 °C for 4 h in Ar, while fibrous products cannot be obtained from heat treatment of hybrid fibres with $C^*:Si = 1.7$. These products are dark grey powders.

The morphology of β -SiC fibres obtained changes with the $C^*:Si$ ratio of the precursor fibres. Fig. 2 shows SEM photographs of β -SiC fibres obtained from the hybrid fibres with $C^*:Si = 2.6$ and 4.3. β -SiC fibres obtained from the precursors with $C^*:Si = 2.6$ are curled and coarse [Fig. 2(a)]. The morphology of β -SiC fibres obtained from the precursors with $C^*:Si = 3.4$ and 5.4 is similar to that from the precursors with $C^*:Si = 4.3$ [Fig. 2(b)]. They are finer than β -SiC fibres formed from the hybrid fibres with $C^*:Si = 2.6$, although pinholes are observed on their surfaces. These facts suggest that the $C^*:Si$ ratio of the hybrid fibres is an important factor in determining the morphology of β -SiC fibres as well as their formation.

The salient features of this procedure for producing continuous β -SiC fibres are the use of relatively low-cost starting materials and the avoidance of troublesome steps. The silica gel-phenolic resin hybrid fibres spun from acidic ethanolic solutions of TEOS and phenolic resins can be converted into β -SiC fibres just by heat treatment at 1500 °C for 4 h in Ar when $C^*:Si \geq 2.6$ for the hybrid fibres.

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