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Ceramics International 25 (1999) 523–527

CERAMICS
INTERNATIONAL

Inorganic–organic hybrid route to synthesis of ZrC and Si–Zr–C fibres

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Received 7 May 1997; accepted 4 August 1997

Abstract

ZrO_2–phenolic resin and SiO_2–ZrO_2–phenolic resin hybrid fibres have been prepared by sol–gel processing using zirconium tetrakis(2,4-pentanedionate) (ZTP), tetraethoxysilane (TEOS), and novolac-type phenolic resins as raw materials. ZTP and the phenolic resins dissolved in a mixture of ethanol and 2,4-pentanedione have undergone a sol–gel reaction to give ZrO_2–phenolic resin hybrid fibres when H_2O and H_2SO_4 have been added to the solutions at a H_2O/Zr molar ratio of 0.45 and H_2SO_4/Zr molar ratio of 0.66. On the basis of the molar ratios and the H_2O/Si and H_2SO_4/Si molar ratios of solutions, which were demonstrated to be optimal for preparing SiO_2–phenolic resin hybrid fibres from TEOS and the phenolic resins, amounts of H_2O and H_2SO_4 to be added to TEOS-ZTP-phenolic resin–H_2O–H_2SO_4–ethanol–2,4–pentanedione solutions with numerous Si-to-Zr atomic ratios have been estimated. The solutions containing the estimated amounts of H_2O and H_2SO_4 have been found to give SiO_2–ZrO_2–phenolic resin hybrid fibres with Si-to-Zr ratios which correspond to those of the solutions, meaning that the hybrid fibres with a variety of Si-to-Zr atomic ratios can be prepared by this estimation method. The hybrid fibres have been convertible into ZrC or Si–Zr–C fibres upon firing at 1500°C for 4 h in an Ar flow. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

1. Introduction

Silicon-based non-oxide ceramic fibres are important reinforcement materials for various types of composites since the fibres show high tensile strength and thermal stability [1]. SiC (Nicalon) and Si–Ti–C–O (Tyranno) fibres have been commercially fabricated using polycarbosilanes and polytitanocarbosilanes, respectively, as precursors.

The fibres, however, are quite expensive. This is due to the cost of the precursors and necessity of some additional steps for the fibre synthesis, such as cure. Therefore, development of another route to produce this group of fibres would be necessary for their cost-effective fabrication.

Sol–gel processing is one of various procedures for manufacturing fibres, by which synthesis of oxide fibres, such as silica fibres, have been demonstrated [2]. In addition, inorganic–organic hybrids produced by sol–gel processing have been demonstrated to act as precursors of non-oxide ceramic powders [3]. Then, inorganic–organic hybrid fibres, prepared by the processing, are expected to be useful precursors for non-oxide ceramic fibres. In our previous studies, we have shown that SiC [4,5], Si_3N_4 [6], and Si–Ti–C fibres [7,8] can be produced from the hybrid fibres.

Regarding preparation of SiO_2–TiO_2–phenolic resin hybrid fibres as precursors for Si-Ti-C fibres from tetraethoxysilane [$Si(OC_2H_5)_4$, TEOS], titanium tetrakis(2,4–pentanedionate), and novolac-type phenolic resins [8], we described that the amounts of water and acid added to the starting solutions play important roles in appearance of spinnability of the solutions just before the gelation; the amounts have to be varied as a function of Si-to-Ti atomic ratios of the solutions to obtain the fibres with different Si-to-Ti ratios. And, the amounts which are optimal for spinning the hybrid fibres were found to be in proportion to the Si-to-Ti atomic ratio of the solutions. This fact further suggested that these amounts may be estimated just from the amounts suitable for producing SiO_2–phenolic resin and TiO_2–phenolic resin hybrid fibres without investigating those for each solution with a different Si-to-Ti atomic ratio.

Consequently, this study has been aimed at investigating whether such proportional relations between the

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PII: S0272-8842(97)00089-8

water and acid amounts and the metal composition of solutions can be estimated under optimal conditions for producing alternative hybrid fibres consisting of two inorganic oxide and phenolic resin components. For this purpose, the SiO_2–ZrO_2–phenolic resin system has been elected in this study. At first, reaction conditions for producing ZrO_2–phenolic resin hybrid fibres have been investigated to clarify suitable amounts of water and an acid to be added to their starting solutions. Then, attempts have been made to produce SiO_2–ZrO_2–phenolic resin hybrid fibres with various Si-to-Zr atomic ratios on the basis of the reaction conditions. Conversion of the hybrid fibres into carbide fibres has also been studied.

2. Experimental Procedure

2.1. Materials

TEOS (Nacalai Tesque, Inc.) and zirconium tetrakis(2,4-pentanedionate) ($Zr(C_5H_7O_2)_4$, ZTP, Matsumoto Seiyaku Co.) were used as a Si and a Zr source, respectively. Novolac-type phenolic resins used were supplied by Gun-ei Kagaku Kogyo Co. (PSM-2317 [5]). Sulfuric acid (H_2SO_4) was used as acid catalyst for the hydrolysis and polycondensation of TEOS and ZTP. A mixture of ethanol and 2,4-pentanedione was applied as solvent.

2.2. Preparation of starting solutions

Starting solutions for synthesizing ZrO_2–phenolic resin hybrid fibres were prepared by dissolving ZTP and the phenolic resins in a mixture of ethanol (10 cm^3) and 2,4–pentanedione (10 cm^3), followed by the addition of distilled water and H_2SO_4. The amount of ZTP dissolved in the solutions was fixed at 8.2×10^{-3} mole. The C*/Zr ratio (the atomic ratio of C in the phenolic resins to Zr) of the solutions was fixed at 4.0 since SiO_2–phenolic resin hybrid fibres prepared from solutions with C*/Si ratios of 3.0–4.0 gave SiC fibres with a low free carbon content of ca. 1.6 wt% [5]. The amounts of H_2O and H_2SO_4 added to the solutions were indicated as the H_2O/Zr and H_2SO_4/Zr molar ratios, respectively.

The solutions were at first stirred at room temperature for 30 min, and then soaked at 65°C. The viscosity of the solutions increased with time, giving viscous sols from which fibres could be spun by immersing glass rods into the sols and pulling them up.

Starting solutions for producing SiO_2–ZrO_2–phenolic resin hybrid fibres were prepared in a similar way to the above using TEOS as a SiO_2 source additionally. The total amount of TEOS and ZTP in the solutions was fixed at 8.2×10^{-3} mole, and the C*/(Si + Zr) ratio at 4.0.

The fibres prepared by the sol–gel reactions were sticky, which is attributed to the inclusion of solvent. In order to avoid coalescence of the fibres, they were dried at room temperature at least overnight.

2.3. Heat-treatment of the hybrid fibres

The dried fibres were placed on alumina boats without further pretreatment and fired at 1100–1500°C for 4 h in flowing Ar (100 $cm^3 min^{-1}$) in a tube furnace. The heating rate was ca. 10°C min^{-1}.

2.4. Analytical procedures

Hybrid fibres prepared by the sol–gel reactions were characterised with a Perkin–Elmer System 2000 FT-IR spectrometer under an N_2 flow. The C*/Zr or C*/(Si + Zr) ratios of the fibres was estimated from their TG curves obtained with a Shimadzu TGA-50H. The procedure for the determination was similar to that for determining C*/(Si + Ti) ratios of SiO_2–TiO_2–phenolic resin hybrid fibres, which was described in a previous paper [7]. The Si/Zr ratio of the fibres and those formed by the heat-treatment was determined by EDX analysis using a Horiba EMAX-2770 combined with a TOPCON ABT-60 scanning electron microscope. The conditions for the analysis were the same as those described elsewhere [7]. The XRD patterns of powdered samples of the fibrous products obtained by the heat-treatment in Ar were recorded on a Rigaku RAD III-A diffractometer using Cu K_α radiation.

3. Results and discussion

3.1. Synthesis of ZrO_2–phenolic resin hybrid fibres

The spinnability of fibres from ZTP–phenolic resin–H_2O–H_2SO_4–ethanol–2,4-pentanedione solutions varied with their H_2O/Zr and H_2SO_4/Zr ratios. As a result, the spinnability was optimum for the solution with a H_2O/Zr ratio of 0.45 and a H_2SO_4/Zr ratio of 0.66, which yielded fibres over 50 cm in length after ca. 9 h soaking at 65°C. It should be noted that the solution with a H_2O/Zr ratio of 0 and a H_2SO_4/Zr ratio of 0.66 gave only short fibres. This means that the addition of a small amount of H_2O to the solutions is necessary for preparing long fibres.

Fig. 1(a) shows FT-IR spectrum of the fibres obtained, whereas Fig. 1(c) shows that of the phenolic resins. Comparing these spectra, it is seen that major bands due to the phenolic resins are observed at 759, 829 (C-H out-of-plane deformation), 1537 (C = C stretching in aromatic rings), 1657–1996 (over and combination tones of C–H out-of-plane deformation) cm^{-1} in the spectrum shown in Fig. 1(a), indicating the presence of the phenolic resin component in the fibres prepared.

The Zr–O–Zr bond is reported to give rise to a band at 666 cm^{-1} [9]. However, a band due to CO_2 appears at the same wavelength. Then, the FT-IR spectroscopic measurement was conducted under a N_2 flow, as is evidenced from the fact that the intensity of another band due to CO_2 at 2350 cm^{-1} is weak. A band is actually seen at 666 cm^{-1} in Fig. 1(a), which can be assigned to the Zr–O–Zr bond. EDX analysis of powders formed by heating the fibres at 700°C under an additional O_2 flow at a rate of 3 cm^3 min^{-1} indicated the presence of Zr and O. From these facts, it can be stated that the fibres obtained are hybrid fibres consisting of ZrO_2 and phenolic resin components.

3.2. Synthesis of SiO_2–ZrO_2–phenolic resin hybrid fibres

As described above, ZTP–phenolic resin–H_2O–H_2SO_4–ethanol–2,4-pentanedione solutions give ZrO_2–phenolic resin hybrid fibres when the H_2O/Zr ratio is 0.45 and the H_2SO_4/Zr ratio is 0.66. In addition, it was shown in our previous study [8] that optimal spinnability of SiO_2–phenolic resin hybrid fibres is achieved from solutions of TEOS and the phenolic resins containing H_2O and H_2SO_4 at a H_2O/Si ratio of 1.75 and a H_2SO_4/Si ratio of 0.01. From these ratios, H_2O/(Si + Zr) and H_2SO_4/(Si + Zr) ratios of solutions for preparing SiO_2–ZrO_2–phenolic resin hybrid fibres are estimated as below.

For estimation of a H_2O/(Si + Zr) ratio effective for preparing the hybrid fibres from the solution with a given Si/Zr ratio, a graph with the mole fraction of Si, converted from the Si/Zr ratio, of the solution as abscissa and the H_2O/(Si + Zr) ratio as ordinate is used. The values of H_2O/(Si + Zr) ratios, 0.45 and 0.75, are plotted at the fractions of 0 and 100%, respectively. Then, these points are linked by a straight line. The estimation of the H_2O/(Si + Zr) ratio is made using the straight line. For example, the H_2O/(Si + Zr) ratio of the solution with a Si/Zr ratio of 1.0 is appraised to be 1.1 from the graph as shown in Fig. 2(a). Similarly, another graph is drawn for the linear relationship between the Si/Zr ratio and the H_2SO_4/(Si + Zr) ratio, as shown in Fig. 2(b), from which the amount of H_2SO_4 is estimated. Consequently, we prepared the starting solutions with Si/Zr ratios of 1/3, 1.0, and 3.0 by adding H_2O and H_2SO_4 whose amounts were estimated as described above.

These solutions gave viscous sols after soaking at 65°C for 7–9 h, from which fibres, over 50 cm in length, could be drawn. FT-IR spectrum of the fibres obtained

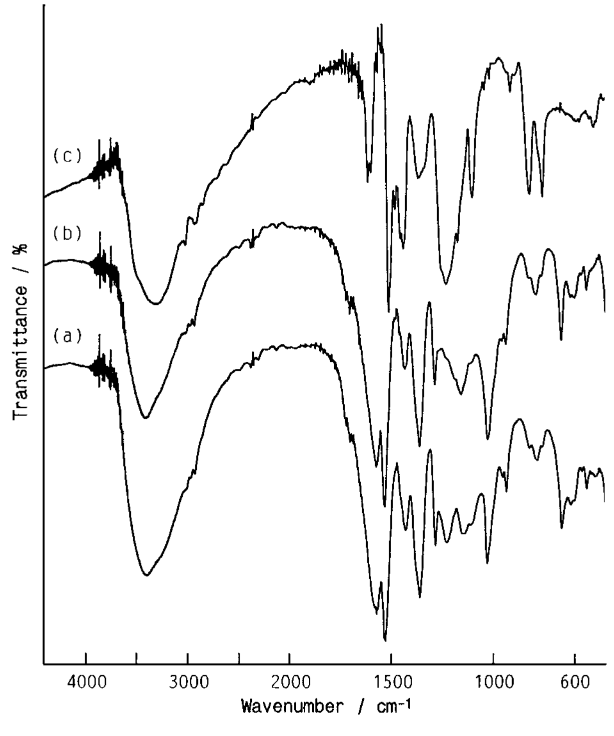

Fig. 1. The FT-IR spectra of (a) ZrO_2–phenolic resin hybrid fibres, (b) SiO_2–ZrO_2–phenolic resin hybrid fibres prepared from starting solutions with a Si/Zr ratio of 1.0, and (c) the phenolic resins. Bands at 759, 829, 1537, 1657–1996 cm^{-1} in (a) and (b) are due to the phenolic resins.

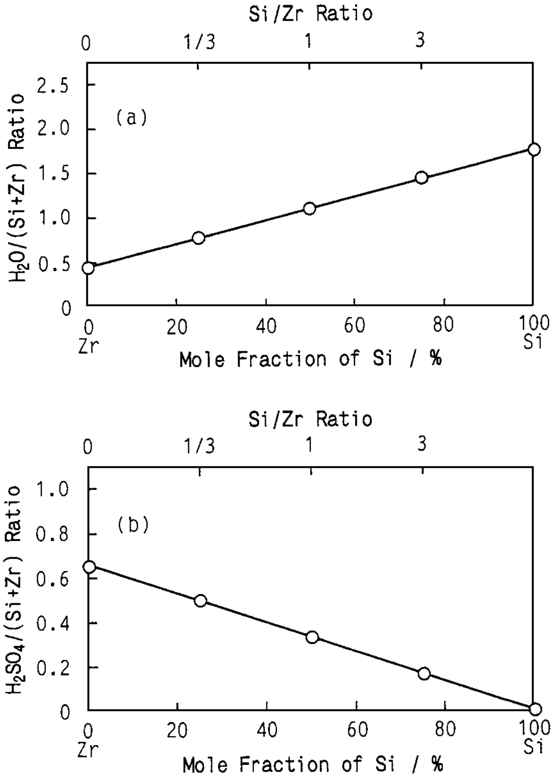

Fig. 2. (a) H_2O/(Si + Zr) and (b) H_2SO_4/(Si + Zr) ratios of starting solutions for producing SiO_2 and/or ZrO_2–phenolic resin hybrid fibres applied in this study.

from the solution with a Si/Zr ratio of 1.0 is shown in Fig. 1(b). Bands due to the phenolic resin and ZrO_2 components are observed in the spectrum. In addition, a band is observed at $1100\,cm^{-1}$, which cannot be seen in Figs. 1(a) and (c). The band is ascribed to the Si–O–Si stretching vibration. Presence of Si, Zr, and O in the powders formed by pyrolysis of the fibres at 700°C in an O_2 flow is demonstrated by EDX. These facts indicate that the fibres involve the SiO_2, ZrO_2, and phenolic resin components. In other words, SiO_2–ZrO_2–phenolic resin hybrid fibres can be prepared with the estimated amounts of H_2O and H_2SO_4 without investigating these amounts suitable for drawing fibres from each solution with a different Si/Zr ratio.

The Si/Zr and C*/(Si + Zr) ratios of the SiO_2–ZrO_2–phenolic resin and ZrO_2–phenolic resin hybrid fibres are shown in Table 1. The Si/Zr ratio of the fibres is not equal to that of their starting solution. However, the ratio of the hybrid fibres varies with that of the solution in a similar manner, implying that the Si/Zr ratio of the hybrid fibres is adjustable with the amounts of TEOS and ZTP dissolved in the starting solution. The C*/(Si + Zr) ratio of the hybrid fibres is larger than that of the starting solution, which would result from inclusion of the solvent and/or low boiling components of the solution in the fibres.

3.3. Heat-treatment of the hybrid fibres in Ar

The SiO_2–ZrO_2–phenolic resin hybrid fibres, prepared from the solution with a Si/Zr ratio of 1.0, were heated at 1100–1500°C in Ar for 4 h. Products obtained after the heat-treatment preserved the fibrous form regardless of the heating temperature. Their XRD patterns are shown in Fig. 3. The fibrous products formed by the heat-treatment at 1100, 1200, and 1250°C give rise to broad peaks (Fig. 3(a)–(c), respectively), which would be due to orthorhombic and monoclinic ZrO_2 with low crystallinity. Sharp peaks in Fig. 3(d) are due to ZrC, indicating that formation of ZrC takes place on heating at 1300°C, although SiC is not yielded at the temperature.

Peaks due to β-SiC phases are observed in the XRD pattern of the fibrous products formed by the treatment at 1500°C (Fig. 3(f)), meaning that the conversion from the SiO_2–ZrO_2–phenolic resin hybrid fibres to Si–Zr–C fibres is complete by firing at 1500°C for 4 h. A SEM photograph of the Si–Zr–C fibre is shown in Fig. 4.

Table 1
Si/Zr and C*/(Si + Zr) ratios of ZrO_2–phenolic resin and SiO_2–ZrO_2–phenolic resin hybrid fibres prepared from starting solutions with a C*/(Si + Zr) ratio of 4.0

Si/Zr ratio of starting solutions	Si/Zr ratio of hybrid fibres	C*/(Si + Zr) ratio of hybrid fibres
Zr only	Zr only	5.1
1/3	0.36	5.5
1.0	0.91	5.9
3.0	2.36	5.7

SiO_2–ZrO_2–phenolic resin hybrid fibres prepared from the solutions with Si/Zr ratios of 1/3 and 3.0 and ZrO_2–phenolic resin hybrid fibres also yielded fibrous products after heating at 1500°C in Ar for 4 h. Their XRD patterns (Fig. 5) indicate the formation of Si–Zr–C and ZrC fibres. The Si/Zr ratio of the Si–Zr–C fibres obtained, shown in Table 2, is slightly lower than, but almost consistent with that of the starting solutions.

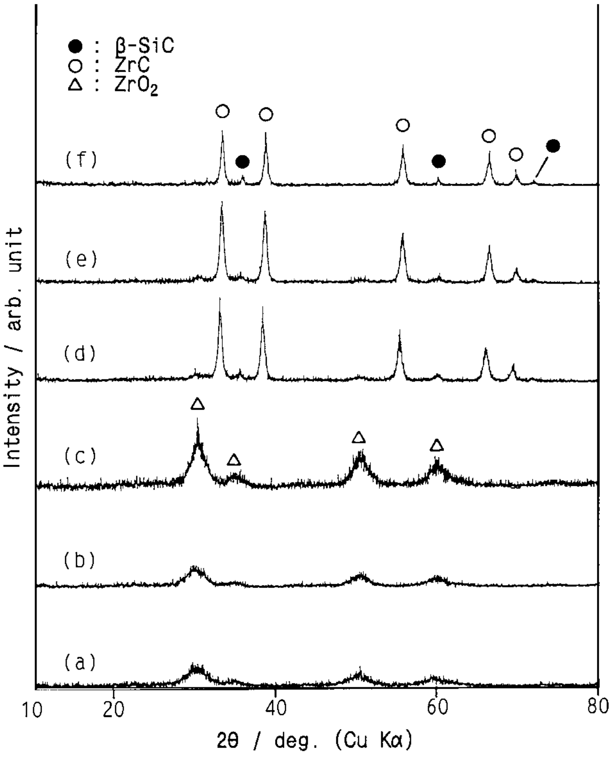

Fig. 3. The XRD patterns of fibrous products obtained by heating SiO_2–ZrO_2–phenolic resin hybrid fibres, prepared from starting solutions with a Si/Zr ratio of 1.0 and a C*/(Si + Zr) ratio of 4.0, at (a) 1100, (b) 1200, (c) 1250, (d) 1300, (e) 1400, and (f) 1500°C in Ar for 4 h.

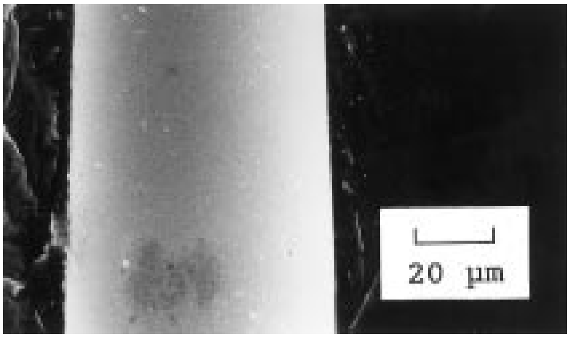

Fig. 4. A SEM photograph of a Si–Zr–C fibre with a Si/Zr ratio of 0.92.

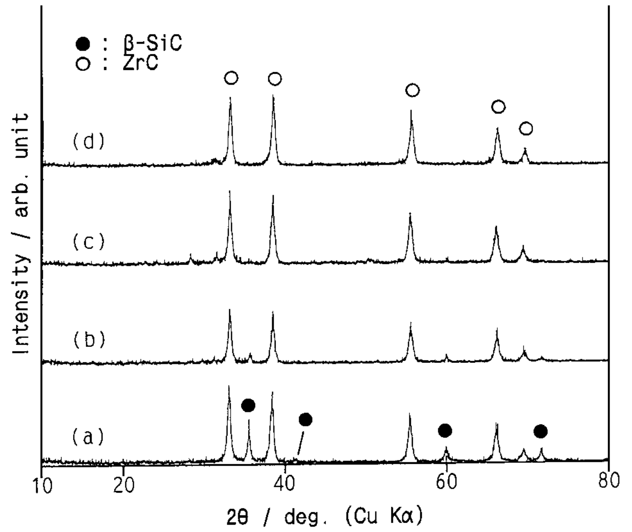

Fig. 5. The XRD patterns of fibrous products obtained by heat-treatment at 1500°C in Ar for 4 h of SiO_2–ZrO_2–phenolic resin hybrid fibres prepared from starting solutions with a Si/Zr ratio of (a) 3.0, (b) 1.0, and (c) 1/3, and (d) ZrO_2–phenolic resin hybrid fibres. The C*/(Si + Zr) ratio of the starting solutions is 4.0.

Table 2
Si/Zr ratios and ceramic yields of ZrC and Si–Zr–C fibres obtained by the heat-treatment at 1500°C in Ar for 4 h

Si/Zr ratio of starting solutions	Si/Zr ratio of Si–Zr–C fibres	Ceramic yield (%)
Zr only	Zr only	41.9
1/3	0.28	37.0
1.0	0.92	36.1
3.0	2.55	39.5

This suggests that the Si/Zr ratio of the carbide fibres is actually adjustable with the amounts of TEOS and ZTP used for the preparation of the starting solutions. The ceramic yield of the carbide fibres is ca. 39 % on the average (Table 2).

In short, it is shown that Si–Zr–C fibres with various Si/Zr ratios can be produced by heat-treatment of SiO_2–ZrO_2–phenolic resin hybrid fibres, prepared from TEOS–ZTP–phenolic resin–H_2O–H_2SO_4–ethanol–2,4-pentanedione solutions by sol–gel processing, at 1500°C in Ar for 4 h. The Si/Zr ratio of the fibres depends on that of the starting solutions. This means that the Si/Zr ratio can easily be adjusted by the molar ratio of TEOS and ZTP in the starting solutions. With the molar ratio, however, the amounts of H_2O and H_2SO_4 to be added to the solutions have to be varied in order to make them spinnable just before the gelation. It is troublesome to investigate these amounts for each solution with a different Si/Zr ratio. As was described in section 3.2, however, these amounts can easily be estimated from those suitable for SiO_2–phenolic resin and ZrO_2–phenolic resin hybrid fibres.

4. Conclusions

Synthesis procedures were described for ZrO_2–phenolic resin and SiO_2–ZrO_2–phenolic resin hybrid fibres as precursors for ZrC and Si–Zr–C fibres, respectively. ZTP–phenolic resin–H_2O–H_2SO_4–ethanol–2,4–pentanedione solutions with a H_2O/Zr ratio of 0.45 and a H_2SO_4/Zr ratio of 0.66 were found to give ZrO_2–phenolic resin hybrid fibres by soaking them at 65°C for ca. 9 h. It was revealed that the amounts of H_2O and H_2SO_4 to be added to TEOS–ZTP–phenolic resin–H_2O–H_2SO_4–ethanol–2,4-pentanedione solutions for preparing the SiO_2–ZrO_2–phenolic resin hybrid fibres with various Si/Zr ratios could be easily estimated from those optimal for producing SiO_2–phenolic resin and ZrO_2–phenolic resin hybrid fibres. The hybrid fibres could be converted into the carbide fibres by the heat-treatment at 1500°C in Ar for 4 h. The Si/Zr ratio of the SiO_2–ZrO_2–phenolic resin and Si–Zr–C fibres was found to depend on that of the starting solutions.

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