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Improvement of the temperature resistance of aluminium-matrix composites using an acid phosphate binder

Part II *Preforms*

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A preform consisting of a reinforcement and a small proportion of a binder is infiltrated with a liquid metal in order to form a metal-matrix composite. This paper (Part II) reports on the preparation and characterization of preforms of SiC whiskers and of short carbon fibres. Both types of preform were prepared by wet forming, using either a silica binder or an acid phosphate binder (with the P/Al atom ratio ranging from 1–23), and using either water or acetone as the liquid carrier during wet forming. The dependence of the compressive strength of the preform on the binder species, binder quantity and preform heat-treatment temperature (up to 1200 °C) and atmosphere (air or argon) is presented. For SiC whisker preforms made by using an acid phosphate binder containing excess phosphoric acid, the binder–SiC reaction product, SiP_2O_7, was primarily responsible for increasing the compressive strength of the preform. The SiC whisker preforms made by using the phosphate binders generally had higher compressive strengths than those of preforms made by using the silica binder after heat treatment at 500 °C or above. The compressive failure of the SiC whisker preforms made with the phosphate binders was in shear, whereas the failure of the SiC whisker preforms made by using the silica binder involved lateral surface buckling. This difference is due to the more uniform binder distribution in preforms made with the phosphate binders. Thus, preforms made with the phosphate binders have better machinability and are stronger. The determining parameters for the compressive strength of the SiC whisker preforms are the relative amount of the binder and the relative reactivity between the SiC whiskers and the binder. The crystallinity, phase and morphology of the binders showed little effects. The relative reactivity increased with increasing temperature if the binder and heating environment were fixed. The relative reactivity increased with increasing P/Al atom ratio. In the SiC whisker preforms made with different phosphate binders after heat treatment at the same temperature, the relative amount of the binder played a more important role than the relative reactivity.

1. Introduction

This paper (Part II) evaluates SiC whisker and short carbon fibre preforms made with silica and acid phosphate binders. The dependence of the compressive strength of the preform on the binder species, binder quantity and preform heat-treatment temperature is presented. For information on the binders by themselves, readers are referred to Part I of this series [1]. Information on the aluminium-matrix composites resulting from the preforms is given in Part III [2].

2. Reinforcements

A wide variety of ceramic, boron and carbon materials are used as reinforcements for metals. Silicon carbide is currently the most commonly used reinforcement in aluminium–matrix composites, due to its commercial availability and excellent properties, although aluminium oxide (Al_2O_3), boron carbide (B_4C) and graphite are also common, especially in the aerospace industry. SiC is extremely hard and strong. It also has good abrasion, corrosion, erosion, thermal shock and oxidation resistance. In addition to the high strength and modulus of elasticity, SiC whiskers also show a high thermal conductivity and a low coefficient of thermal expansion compared to many other ceramics.

Crystalline SiC has two forms, α and β. In particular, α-SiC consists of six different forms, I–VI. The α-SiCs are typically based on either rhombohedral or hexagonal lattices. The α-SiC whiskers (Form IV) used were SILAR SC-9 supplied by Advanced Composites Materials Corporation. The average diameter was 0.6 μm and the length was 10–80 μm. The whisker content ranged from 80%–90%.

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Chopped carbon fibres were employed in this work to study the potential of improving the temperature resistance of carbon fibre-reinforced metal-matrix composites (MMCs) with the variation of the binder species in the preparation of preforms. Carbon fibres have the advantages of high strength, high modulus of elasticity and very low density. Other attractive properties of carbon fibres are their low thermal expansion coefficient and high thermal conductivity. The chopped carbon fibres used in this work were Ashland Petroleum's Carboflex P-100. They were pitch-based, unsized, and of length about 100 μm and diameter 10 μm.

3. Preform preparation

The fabrication of the SiC whisker preforms was performed by wet forming. After making a slurry by mixing SiC whiskers with the binder, wet forming was performed using a hydraulic press at a pressure of 4.0 MPa. The drying of the preforms was carried out in air at 200 °C for 24 h. Table I shows the weight fraction of binder in the resulting preforms, which all contained 22 vol % whiskers after drying at 200 °C. The binder weight fraction was about 4.2 wt % for all preforms with the phosphate binders except the preform with the phosphate A23 binder with acetone carrier, but was 2.7 wt % for preforms with the silica binder. This difference between silica and phosphate binders is probably due to the stronger chemical reactivity (with the SiC) and the higher viscosity of the phosphate binders. That the SiC whisker preform made by using 1 part of the phosphate A23 solution with 15 parts of acetone (instead of water), showed a highest weight fraction (5.3%) was due to the higher volatility of acetone. The preforms were cylindrical, with diameter 40 mm and height 20 mm.

TABLE I Binder content in SiC whisker preforms after drying at 200 °C

Binder	Weight fraction (wt %)
Silica (water)	2.7 (0.4)[a]
A03 (water)	4.4 (0.4)
A06 (water)	4.0 (0.6)
A23 (water)	4.1 (0.9)
A23 (acetone)	5.3 (0.5)
MAP (water)	4.3 (0.7)

[a] Values in parentheses show the standard deviation.

The drying of the binder in the SiC whisker preforms was complete after heating at 200 °C for 24 h. Four different temperatures, 500, 800, 1100 and 1200 °C, were used for heat treatment of the preforms (with water as the carrier) after drying. The preform with acetone as the carrier was only heat treated at 500 °C. The temperature was increased from room temperature at the rate of 10 °C min^{-1}, kept at the target temperature (500, 800, 1100 or 1200 °C) for 4 h, and then cooled to room temperature at the rate initially of 10 °C min^{-1} and finally (below about 650 °C) at the rate corresponding to furnace cooling (i.e. cooling rate $\leqslant$ 10 °C min^{-1}). When the target temperature was below or equal to 800 °C, the preform was heat treated in air. When the target temperature was at 1100 °C, the preform was heat treated in two different environments, air and argon. When the target temperature was at 1200 °C, the preform was heat treated in argon only.

Table II shows the weight change of the preform after heat treatment relative to the weight after drying. There was essentially no weight loss after heat treatment at 500 or 800 °C for all binders except those of the preforms made by using the phosphate A12 and A23 binders. The weight loss increased from A12 to A23 at both temperatures. In addition, there was a steady increase of weight loss for the preforms made by using the phosphate A12 binder from 500 °C to 800 °C and the phosphate A23 binder from 500, 800 or 1100 °C (in argon) to 1200 °C (in argon). However, no significant weight change was observed for the preforms made by using the silica binder after heat treatment at 500, 800 or 1100 °C (in argon). The weight loss of the phosphate A12 and A23 binders at 500 °C may be due to the formation of a crystalline phase (type A aluminium metaphosphate), which resulted in the release of phosphorus in a certain form.

TABLE II Weight change of SiC whisker preforms

Heat-treatment temperature (°C)	Silica	A03	A06	A12	A23 (water)	A23 (acetone)	MAP
500	0% (0%)[a]	+ 0.2% (0.1%)	+ 0.1% (0.1%)	– 0.6% (0.4%)	– 1.7% (0.7%)	– 1.5% (0.4%)	– 0.2% (0.1%)
800	+ 0.6% (0.4%)	– 0.1% (0.1%)	– 0.2% (0.1%)	– 0.8% (0.4%)	– 2.0% (0.5%)	– –	– –
1100 (air)	+ 13.6% (0.5%)	– –	– –	– –	+ 16.9% (1.7%)	– –	– –
1100 (argon)	– 0.2% (0.2%)	– –	– –	– –	– 3.4% (0.3%)	– –	– –
1200 (argon)	– –	– 2.9% (0.3%)	– –	– –	– 3.5% (0.9%)	– –	– 3.1% (0.5%)

[a] Values in parentheses show the standard deviation.

The weight loss at 500, 800 and 1100 °C (argon) was significant only for the case of the phosphate A23 binder (with water), probably because the phosphate A23 binder had a much higher P/Al atom ratio than the other phosphate binders. A substantial weight increase was observed for the preforms made by using the phosphate A23 binder and the silica binder after heat treatment at 1100 °C in air. This was due to the oxidation of the SiC whiskers, which resulted in the formation of SiO_2, as confirmed by X-ray diffraction (XRD). For the preforms made by using the phosphate A03, A23 and MAP binders, weight loss was observed after heat treatment at 1200 °C in argon. This was probably due to the dissociation of some or all of the $Al(PO_3)_3$(A) crystalline binder into a more stable form (cristobalite $AlPO_4$ [3, 4]) together with a gas phase. The formation of the cristobalite $AlPO_4$ was confirmed by XRD.

The fabrication of carbon fibre preforms was performed also by wet forming. Four binders were used to prepare preforms: silica, phosphate A23, acrylic emulsion and water glass (Na_2SiO_3). After making a slurry by mixing chopped carbon fibres with the binder, wet forming was performed at a pressure of 1 MPa. The resulting preforms after subsequent drying contained an average of 55 vol % (50–60 vol %) carbon fibres. The drying of the preforms was carried out in air at 200 °C for 24 h. The preforms were cylindrical, with diameter 40 mm and height 20 mm.

The much higher filler volume fraction of the carbon fibre preforms (50%–60%) than the SiC whisker preforms (22%) is due to the smaller aspect ratio of the carbon fibre (~ 10) compared to that (20–150) of SiC whiskers. The volume fraction of 55% approaches the value generally obtained for powder preforms, in which the powder particles typically have an aspect ratio of 1–5.

A purpose of this work was to investigate which kind of binder was suitable for the preparation of carbon fibre preforms. The compressive strength of the preforms was measured, because it gives information on the binding ability of the binder in the preforms.

Another set of carbon fibre preforms was prepared for use in fabricating composites. Four types of preform were prepared with the silica or phosphate A23 binder. Two of the four types used the same binder/water ratio as in previous cases (silica $\frac{1}{6}$; phosphate A23 $\frac{1}{15}$). The third and fourth types of preform used the phosphate A23 binder with a binder/acetone (no water) ratio of $\frac{1}{15}$ and $\frac{1}{5}$ respectively. Table III shows the binder content of the carbon fibre preforms used for fabricating MMCs. That the preform with the silica binder/water ratio of $\frac{1}{15}$ had a smaller binder content than that with the phosphate A23 binder/water ratio of $\frac{1}{15}$ was due to the higher viscosity of the phosphate A23 binder. The preform made with the phosphate A23 binder/acetone ratio of $\frac{1}{15}$ had a similar binder content to that made with the phosphate A23 binder/water ratio of $\frac{1}{15}$. The binder content of the carbon fibre preform made using the phosphate A23 binder/acetone ratio of $\frac{1}{5}$ was indeed much higher than that with 15 parts of water or acetone. Comparison of Tables III and I shows that the binder content of the SiC whisker preforms was higher than that of the carbon fibre preforms for the same phosphate A23 (water) binder. This is probably due to the higher surface area of the SiC whiskers compared to the carbon fibres.

TABLE III Binder content in chopped carbon fibre preforms after drying at 200 °C

Binder	Weight fraction (wt %)
Silica	1.1 (0.2)[a]
A23 (1:15 water)	1.9 (0.3)
A23 (1:15 acetone)	2.0 (0.2)
A23 (1:5 acetone)	5.3 (0.2)

[a] Values in parentheses show the standard deviation.

The attack of carbon fibres by aluminium results in the formation of aluminium carbide (Al_4C_3), which deteriorates the mechanical properties of the MMCs. One purpose of this work was to investigate the possibility of alleviating this reaction problem by the use of an appropriate binder for the carbon fibre preforms.

The carbon fibre preforms were dried in air at 200 °C for 24 h, whether or not the resulting drying was complete. The samples were then heat treated at an intermediate temperature of 800 °C or at a higher temperature of 1100 °C (except 1000°C for the water glass case). Heating above 200 °C was performed in an atmosphere of argon. This was done so that the carbon fibres would not oxidize. The oxidation of carbon fibres occurs in air at temperatures above about 500 °C. The temperature was increased from room temperature at the rate of 10 °C min^{-1}, kept at the target temperature (800, 1000 or 1100 °C) for 4 h, and then cooled to room temperature at an initial rate of 10°C min^{-1} and finally (when below 650 °C) at the rate corresponding to furnace cooling (i.e. cooling rate $\leqslant$ 10 °C min^{-1}).

4. SiC whisker preform characterization

All the SiC whisker preform samples prepared were strong enough to meet the requirement for net shaping casting. Specifically, the height difference of the preform measured before and after liquid-metal infiltration was within 0.5 mm, which is of the order of the measurable accuracy. This value is less than 2.5% of the height (~ 20 mm) of the preform.

4.1. Compression testing

A property which can describe the binding ability of the binder is the compressive strength of the preform. Microscopically, the individual whiskers intersected one another through the help of the binder to form a three-dimensional network. Because the binder was weak compared to the whiskers, the preform under compression failed at the binder rather than the whiskers.

The compressive strength of SiC whisker preforms (25.4 mm diameter, 25.4 mm height) made with the silica and phosphate A23 binders was measured and compared, as shown in Table IV. The failure mode of all the preforms with the silica binder was lateral surface buckling (i.e. the cylindrical edge broke off like a shell); the failure mode of all the preforms with the phosphate A23 binder was shear. The compressive strength of preforms made with the silica binder increased smoothly with increasing temperature from 200 °C to 800 °C, but increased steeply after heating at 1100 °C in air. The preform made with the silica binder heated at 1100 °C in argon exhibited a smaller compressive strength compared to its counterpart heated in air. The compressive strength of preforms made with the phosphate A23 binder increased smoothly with increasing temperature from 200 °C all the way up to 1100 °C in air. Again the preform with the phosphate A23 binder heated at 1100 °C in argon exhibited a smaller compressive strength compared to its counterpart heated in air. The strongest preform of those mentioned above was obtained by using the phosphate A23 binder and the 1100 °C (in air) heat treatment. Under most heat-treatment conditions, the preform made with the phosphate A23 binder had a higher compressive strength compared to the corresponding preform made with the silica binder.

The compressive strengths of preforms made with five different phosphate binders, namely A03, A06, A12, A23 and MAP, were measured after heating at 500, 800 and 1200°C (in argon), as shown in Table V.

TABLE IV Compressive strength of SiC whisker preforms made by using the silica and phosphate A23 binders

Binder	Heat-treatment temperature (°C)	Compressive strength (MPa)
Silica	200	3.25 (0.37)[a]
	500	3.66 (0.20)
	800	4.29 (0.25)
	1100 (air)	10.52 (0.45)
	1100 (argon)	5.76 (0.25)
Phosphate (A23)	200	1.64 (0.13)
	500	5.93 (0.20)
	800	11.04 (0.20)
	1100 (air)	15.90 (0.15)
	1100 (argon)	7.44 (0.24)

[a] Values in parentheses show the standard deviation.

TABLE V Compressive strength of SiC whisker preforms made by using the phosphate binders

Preform	Compressive strength (MPa)		
	500 °C	800 °C	1200 °C (in argon)
SiC_w(A03)	9.08 (0.23)[a]	11.98 (0.49)	10.52 (0.31)
SiC_w(A06)	6.25 (0.23)	11.67 (0.17)	–
SiC_w(A12)	6.11 (0.18)	11.53 (0.29)	–
SiC_w(A23)	5.93 (0.20)	11.04 (0.20)	7.99 (0.42)
SiC_w(MAP)	6.75 (0.55)	–	9.28 (0.27)

[a] Values in parentheses show the standard deviation.

The failure mode of the preforms made with these binders were all shear. The compressive strength of the preform decreased with increasing P/Al atom ratio, whether the heating was at 500, 800 or 1200 °C (in argon). In other words, the preform made with the phosphate A03 binder (P/Al atom ratio = 3) had the highest compressive strength and the one made with the phosphate A23 binder (P/Al atom ratio = 23) had the lowest compressive strength for every heating condition.

4.2. Scanning electron microscopy and X-ray diffraction

SEM examination was performed on the heat-treated SiC whisker preforms to view the appearance and distribution of the binder in the whisker network. Fig. 1 shows scanning electron micrographs of the centre of preforms with the silica binder after heat treatment at 200, 500 and 800 °C. For all these temperatures, no patches of binder was observed. Fig. 2 shows scanning electron micrographs of preforms with the silica binder after heat treatment in air or argon at 1100 °C. Photographs are shown for the centre (within 1 mm from the centre) and the surface of the circular edge of each preform. The binder was much more abundant on the surface than in the centre for both heating in air and heating in argon. This difference between the surface and the centre was also observed in preforms heated at 200, 500 and 800 °C. As the silica binder mainly resided at the surface, the interior had a much lower binder concentration than the nominal concentration of 3–5 wt % of the preform. Fig. 2 also shows that the binder was much more abundant for the preform heated in air than that heated in argon for both the surface and centre regions.

XRD patterns are shown in Fig. 3 for the surface (with 1 mm from the surface) of SiC whisker preforms with the silica binder heat treated in air at 200, 500, 800 and 1100 °C. Prior to XRD, the sample was ground into powder. Comparison of Fig. 3 and Table II shows that the significant weight increase at 1100 °C in air was due to the formation of SiO_2 (cristobalite).

Fig. 4 shows XRD patterns form four different points along the radius of the SiC whisker preform with the silica binder heat treated at 1100 °C in air. These four different points were equally spaced at a distance of 6.7 mm and were located along a radius from the surface to the centre. Each point had a width of 2 mm along the radius.

Fig. 4 also shows XRD patterns of the surface and centre of SiC whisker preforms with the silica binder heat treated at 1100 °C in argon. The amount of SiO_2 on the surface of the preform was much less (but nonzero) for the preform heated in argon than that heated in air. This is consistent with the nearly zero weight uptake for the preform heated in argon, as shown in Table II.

The weight uptake (for the preform made with the silica binder after heat treatment at 1100 °C in air) in Table II is clearly due to the formation of SiO_2 (cristobalite). The fact that SiO_2 was more abundant

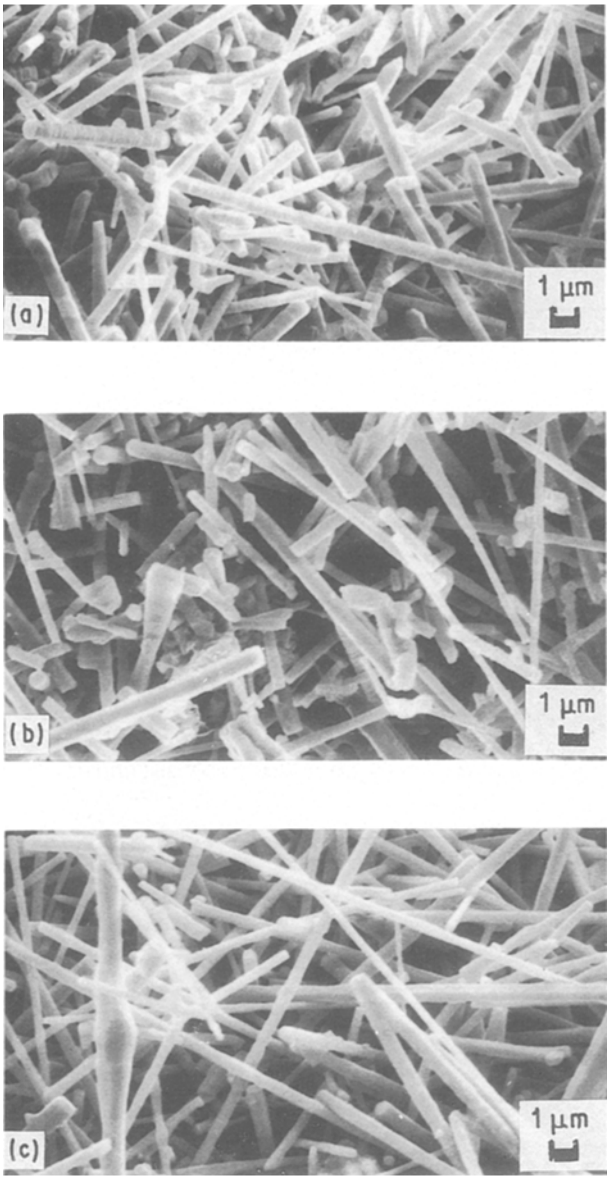

Figure 1 Scanning electron micrographs of the centre of preform with the silica binder after heat treatment in air at (a) 200, (b) 500 and (c) 800 °C.

at the surface for preforms heated in air rather than in argon indicates that air was at least partly responsible for providing the oxygen to react with SiC to form SiO_2. Table IV shows that the SiO_2 formation adds to the binder action, thus increasing the compressive strength of the preforms.

Fig. 5 shows scanning electron micrographs of the centre of SiC whisker preforms with the phosphate A23 binder after heat treatment at 200, 500 and 800 °C in air. No patches of binder were observed, similar to the case of the silica binder. Fig. 6 shows scanning electron micrographs of preforms with the phosphate A23 binder after heat treatment in air or argon at 1100 °C. Photographs are shown for the centre and the surface of the circular edge of each preform. The binder was much more abundant on the surface than in the centre for the preform heated in air, but this difference was not observed for the preform heated in argon. In addition, the binder was more abundant for the preform heated in air than that heated in argon for both the surface and centre regions.

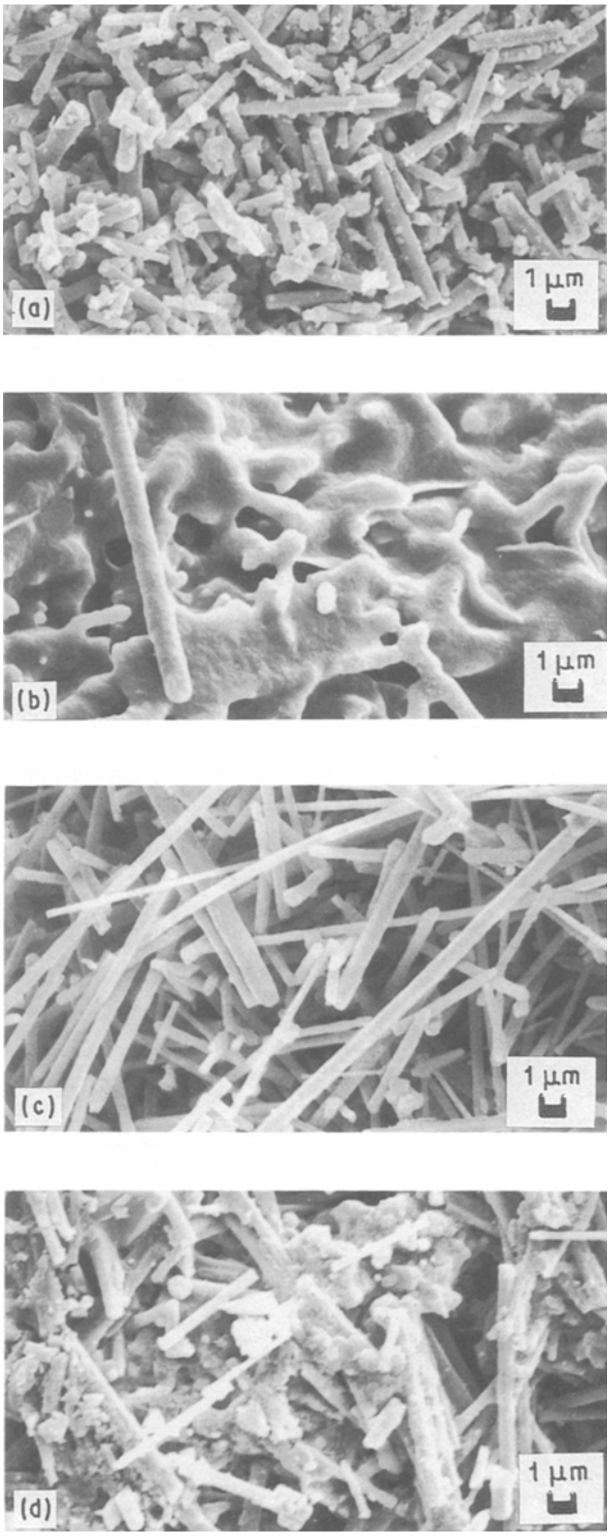

Figure 2 Scanning electron micrographs of preforms with the silica binder after heat treatment in (a, b) air or (c, d) argon at 1100 °C.

XRD patterns for SiC whisker preforms with the phosphate A23 binder are shown in Fig. 7 for the region at the surface (within 1 mm from the surface) of preforms heat treated in air at 200, 500, 800 and 1100 °C. Comparison of Fig. 7 and Table II shows that the significant weight increase at 1100 °C in air was due to the formation of SiO_2 (cristobalite). No phosphate peak was observed, not even at 500 or 800 °C, for which phosphate XRD diffraction peaks were observed from the binder by itself (see Fig. 7 in Part I

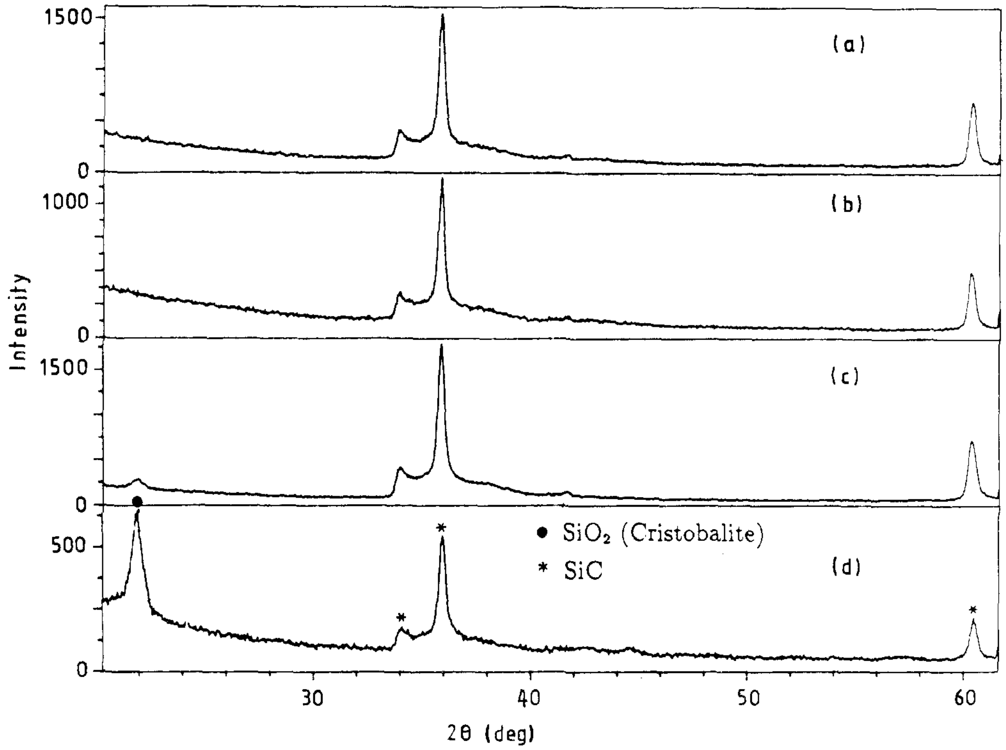

Figure 3 XRD patterns of the surface of preforms with the silica binder heat treated in air at (a) 200, (b) 500, (c) 800 and (d) 1100 °C.

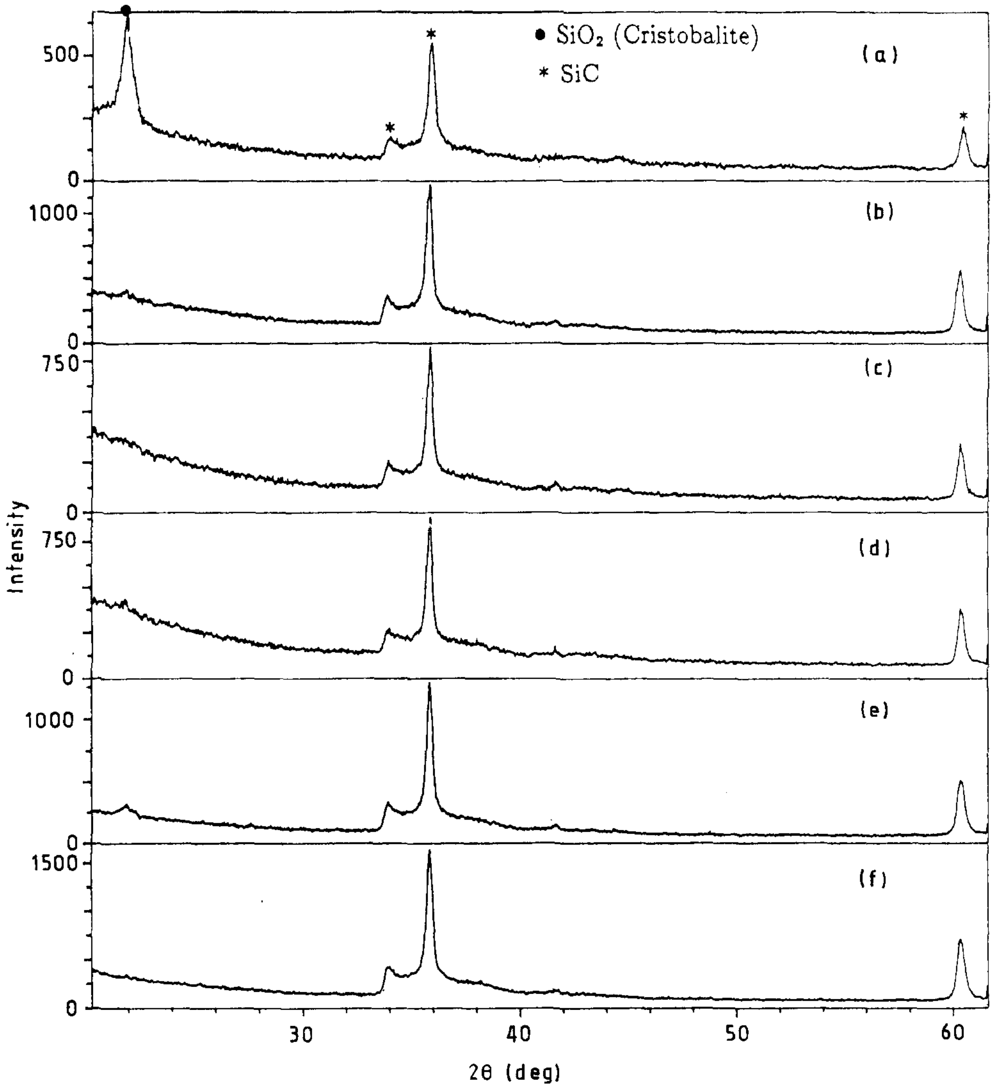

Figure 4 (a–d) XRD patterns from four different points; from (a) the point at the cylindrical edge through two medium points (b and c) to (d) the centre, along the radius of the preform with the silica binder heat treated at 1100 °C in air. (e, f) XRD patterns from the points at (e) the cylindrical edge and (f) the centre of the preform heat treated at 1100 °C in argon.

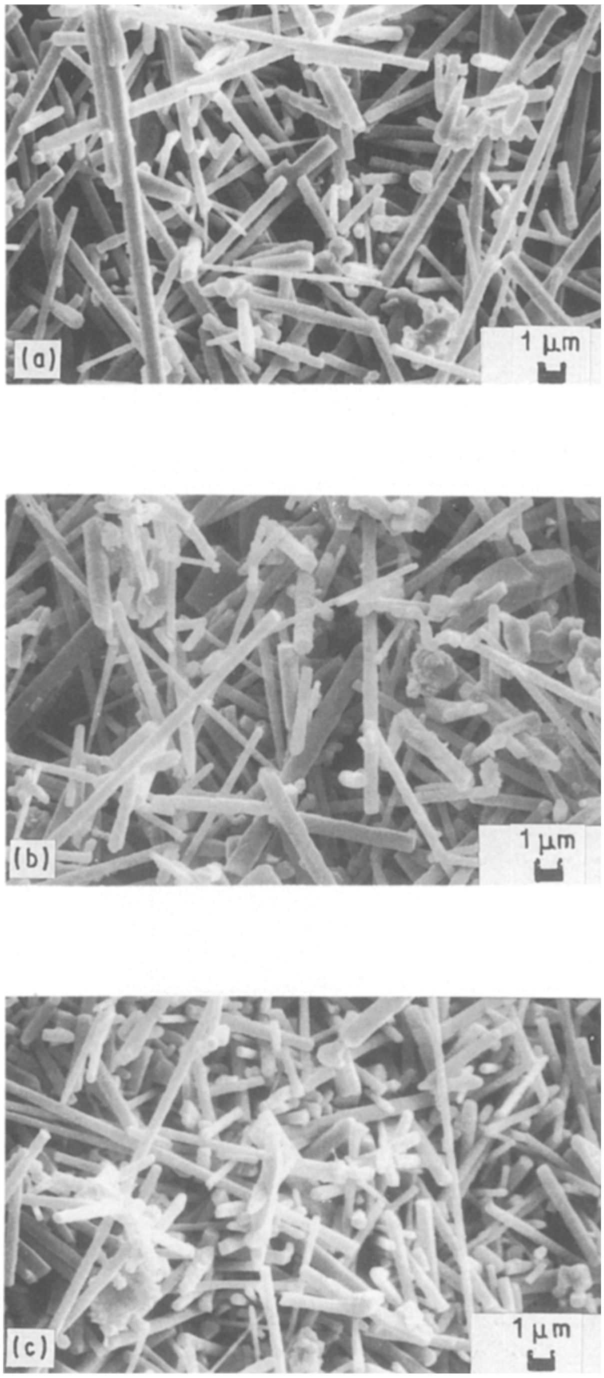

Figure 5 Scanning electron micrographs of the centre of preforms with the phosphate binder A23 after heat treatments in air at (a) 200, (b) 500 and (c) 800 °C.

[1]). This is probably due to the low concentration of phosphate in the preform.

Fig. 8 shows XRD patterns from four different points along the radius of the SiC whisker preform heat treated at 1100 °C in air. These four different points were equally spaced at a distance of 6.7 mm and were located along a radius from the surface to the centre. Fig. 8 shows that SiO_2 was more abundant at the surface than the centre, but the distribution was much more uniform than in the silica binder case (Fig. 4).

Fig. 8 also shows XRD patterns of the surface and the centre of preforms with the phosphate A23 binder heat treated at 1100 °C in air and in argon. The amount of SiO_2 at either the surface or the centre was much less for the preform heated in argon than that heated in air. This is consistent with the lack of a

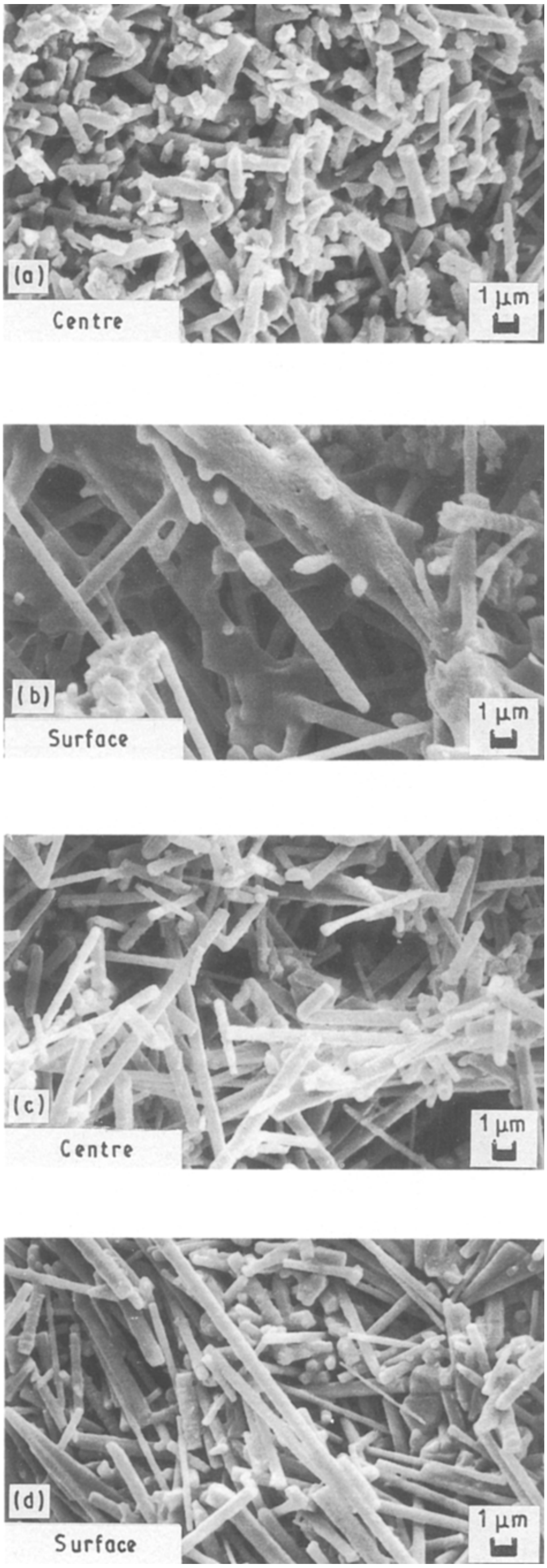

Figure 6 Scanning electron micrographs of preforms with the phosphate A23 binder after heat treatment in (a, b) air or (c, d) argon at 1100 °C.

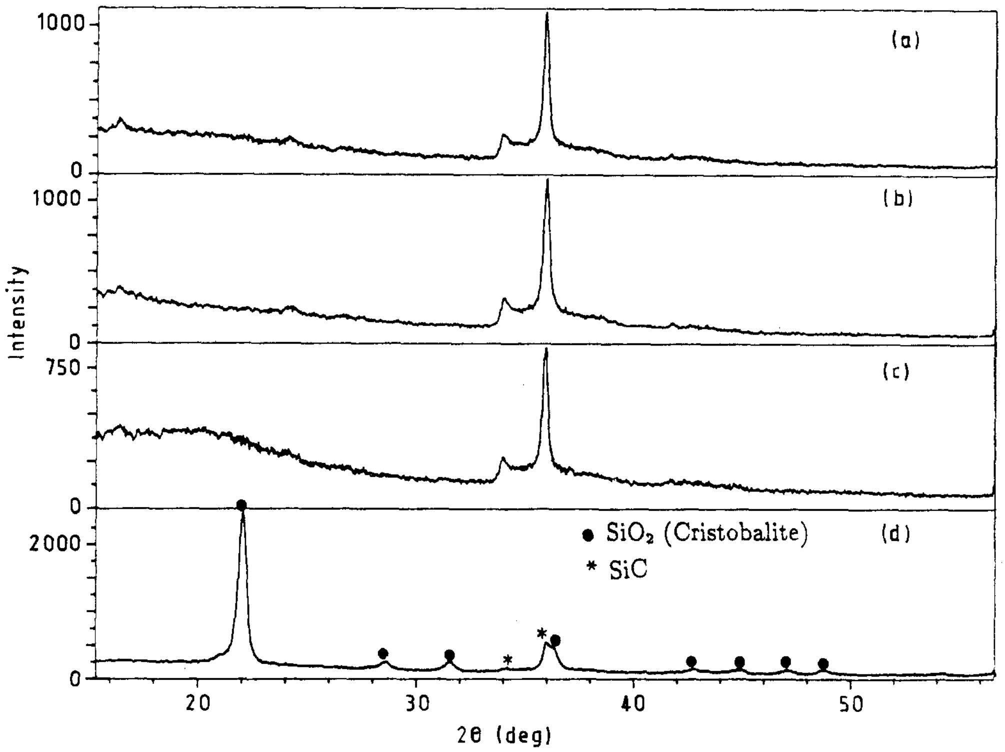

Figure 7 XRD patterns of the surface of preforms with the phosphate A23 binder heat treated in air at 200, 500, 800 and 1100 °C.

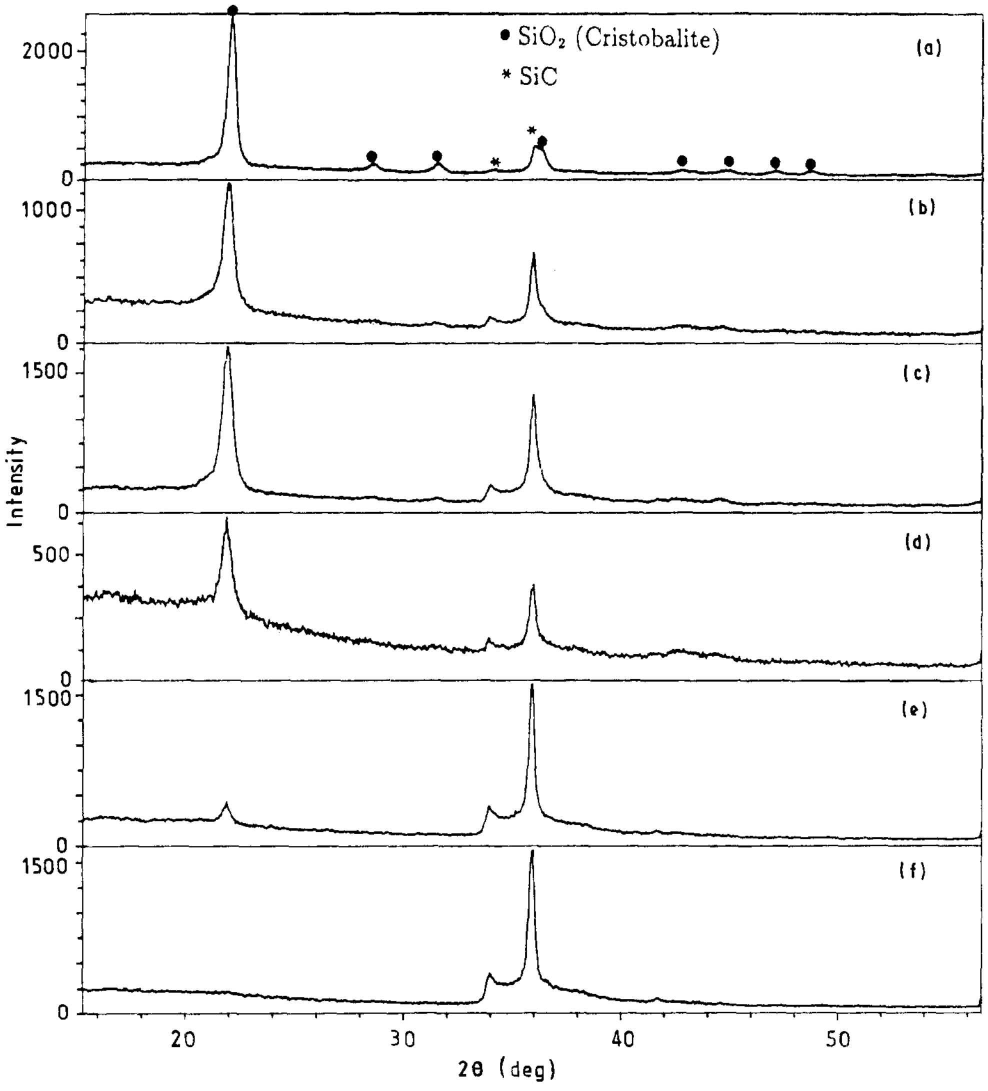

Figure 8 (a–d) XRD patterns from four different points: from (a) the point at the cylindrical edge through two medium points (b and c) to (d) the centre, along the radius of the preform with the phosphate binder heat treated at 1100 °C in air. (e, f) XRD from the points at (e) the cylindrical edge and (f) the centre of the same preform heat treated at 1100 °C in argon.

weight uptake for the preform heated in argon, as shown in Table II.

The scanning electron micrographs of SiC whisker preforms made by using the phosphate A03 binder show the binder clearly at the intersection of the whiskers for the surface of preforms heat treated at 500 °C. The smoothness of the binder between the whiskers is consistent with the smoothness of the binder itself. Again, the binder was more, but not much more, abundant on the surface than in the centre. Similar to the preforms made with the phosphate A23 binder, XRD diffraction showed no phosphate peak after heating at 500 °C, even though phosphate XRD peaks were observed from the binder by itself after heating at 500 °C (see Fig. 4, Part I [1]). This is again attributed to the low concentration of phosphate in the preform.

After the 1200 °C heat treatment in argon, the binder in the SiC whisker preform made with the phosphate A03 binder can be seen clearly at the intersection of the whiskers for the surface and centre of the preform, which again is consistent with the smooth morphology of the binder by itself at the same temperature and in the same environment. In comparison, the binder can be seen clearly at the intersection of the whiskers for the surface but not clearly for the centre region of the preform made by using the phosphate A23 binder after heat treatment at 1100 °C in argon. This is attributed to the smaller binder amount for the phosphate A23 binder case than the phosphate A03 binder case. Again, the XRD pattern of the surface of the preform made by using the phosphate A03 binder after treatment at 1200 °C in argon showed no binder phase for the same reason of low concentration of the binder in the preform.

The scanning electron micrographs and XRD peaks of SiC whisker preforms made with the phosphate binders A06 and MAP after heat treatment at 500 and 1200 °C (in argon) are not shown here because they are similar to those of preforms made with the phosphate A23 binder.

4.3. Local compressive strength and atomic absorption spectrometry

The local compressive strengths of the SiC whisker preforms made by using the silica or the phosphate A23 binders after heating at 800 °C were measured and compared. The specimens were cut out from two regions in each preform. One region, with the specimen dimension of $5 \times 5 \times 6\,\text{mm}^3$, was from the centre of the preform; the other region, with the specimen dimension of $5 \times 3 \times 6\,\text{mm}^3$, was from the surface of the preform, as shown in Fig. 9. Table VI shows the compressive strengths of these local specimens. The surface part of the preform made by using the silica binder had the highest compressive strength, though its centre part had almost no strength at all. This

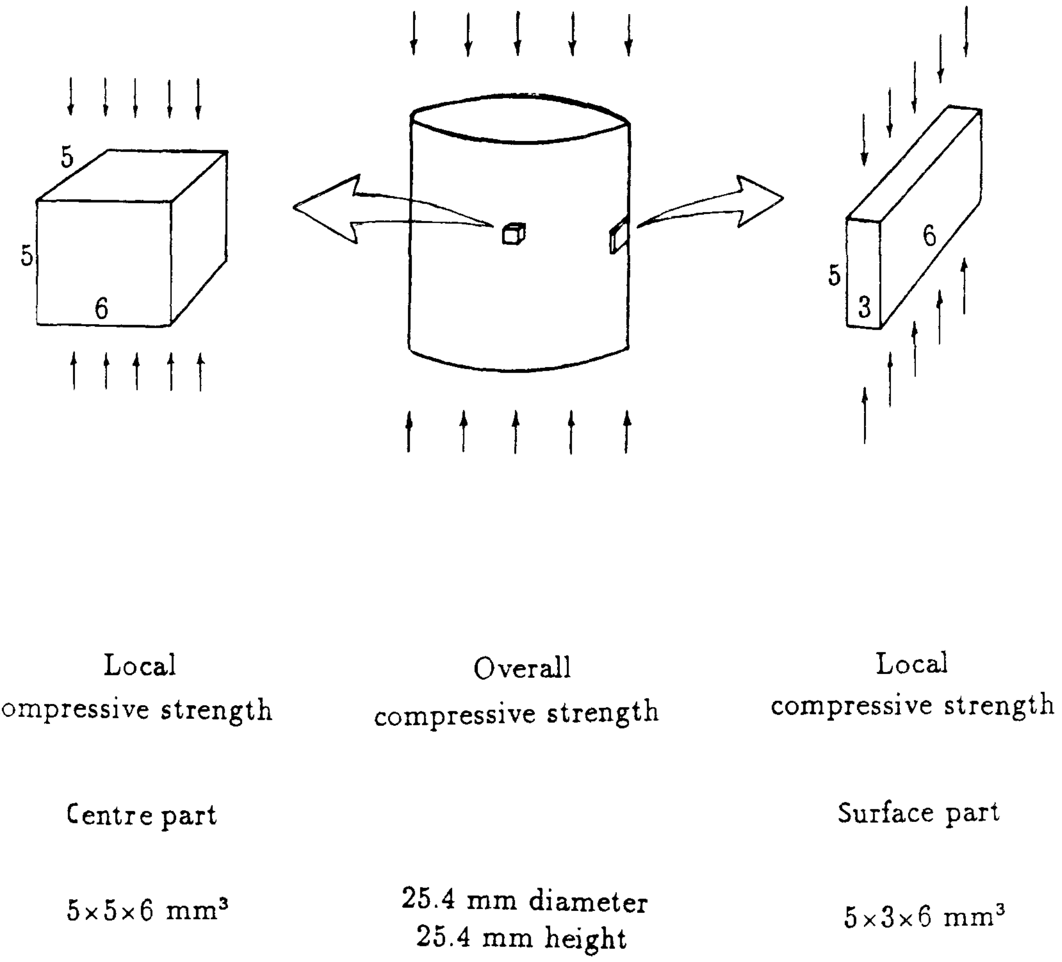

Figure 9 Schematic illustration of the position and geometry of the cut-out local specimen for local compressive testing.

resulted in surface buckling of the whole preform, together with a low overall compressive strength. On the other hand, the surface part of the preform made by using the phosphate A23 binder had only half of the strength of that of the surface part of the preform made by using the silica binder, but the central part of this preform had a strength equal to more than half of that of its surface counterpart. This fact led the whole preform with the phosphate A23 binder to a shear failure, together with a high overall compressive strength.

Atomic absorption analysis was carried out using a Perkin–Elmer 560 Atomic Absorption Spectrophotometer on specimens taken from four different regions along the radius of the SiC whisker preform made with the phosphate A23 binder and heat treated at 500 °C. These four different regions were equally spaced at a distance of 6.7 mm and were located along a radius from the surface to the center, as denoted in sequence as A, B, C and D. Each region had the width of 2 mm along the radius. Table VII and Fig. 10 show the results of the atomic absorption analysis. The preform had large amounts of aluminium and phosphorus in the surface region (A) and lower amounts (but still some, about one-tenth to one-fifth that at the surface) in the other regions (B, C and D). The values of the P/Al atom ratio in Table VII were all higher than 3, which is the ideal value for $Al(PO_3)_3$.

The binder distributions and P/Al atom ratio of the SiC whisker preforms made by using the phosphate A23 binder with water and acetone (Table VII and Fig. 10) are similar.

Comparison of the overall and the local compressive strength and the failure mode of the SiC whisker preforms made by using the phosphate A23 and silica binders suggests a more uniform binder distribution in the preform made with the phosphate A23 binder. The preform made with the silica binder had its binder mostly residing at the surface; this is consistent with the observation that SiO_2 was present significantly at the surface to a depth of ~ 1 mm only.

For confirming the above finding about the binder distribution, an SiC whisker preform made without using any binder was heat treated at 1100 °C in argon. Fig. 11 shows the XRD patterns from four different points along the radius of the preform, equally spaced at a distance of 6.7 mm and located along the radius from the surface to the centre. Each point had a width of 2 mm along the radius. No SiO_2 peak was observed. Therefore, the additional SiO_2 in the preform made by using either silica or phosphate A23 binder after heat treatment at 1100 °C in argon was due to the binder rather than the reaction of the whiskers with the residual oxygen in the chamber. For the silica binder case, the SiO_2 was from the pre-existing silica binder. However, for the phosphate A23 case, the formation of SiO_2 was probably due to the dissociation of the reaction product (silicon phosphate SiP_2O_7, Section 4.4) between the binder and the SiC whiskers. The dissociation of the silicon phosphate resulted in the formation of SiO_2, together with the release of P_2O_5.

An SiC whisker preform made without using any binder was also heat treated at 1100 °C in air. Fig. 12

TABLE VI Local compressive strength of SiC whisker preforms

Binder	Heat treatment (°C)	Local compressive strength (MPa)		
		Surface part	Centre part	Overall
Silica	800	28.1 (3.4)[a]	0.1 (0.0)	4.29 (0.25)
Phosphate A23	800	14.0 (1.5)	8.0 (0.4)	11.04 (0.20)

[a] Values in parentheses show the standard deviation.

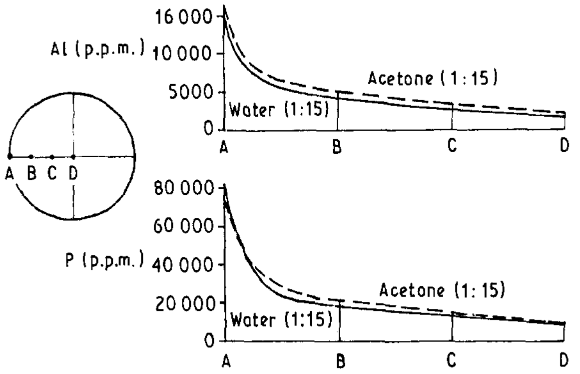

Figure 10 The aluminium and phosphorus concentrations along the radius of the preform made by using the phosphate A23 binder (with water or acetone).

TABLE VII Result of atomic absorption analysis of the SiC whisker preform made by using the phosphate A23 binder (with water or acetone) after heat treatment at 500 °C

Position		Al (p.p.m.) (by weight)	P (p.p.m.) (by weight)	P/Al (by weight)	P/Al (by atom)
Water (1:15)	A	14930 (1980)[a]	81300 (11100)	5.4 (1.0)	4.7 (0.9)
	B	4290 (220)	17800 (1300)	4.1 (0.4)	3.6 (0.3)
	C	2420 (280)	12400 (1400)	5.1 (0.8)	4.5 (0.7)
	D	1660 (230)	8800 (1100)	5.3 (1.0)	4.6 (0.9)
Acetone (1:15)	A	16300 (1260)	74700 (8400)	4.6 (0.6)	4.0 (0.5)
	B	5010 (310)	21700 (1600)	4.3 (0.3)	3.8 (0.3)
	C	3130 (230)	14300 (1200)	4.6 (0.5)	4.0 (0.4)
	D	2060 (190)	9100 (1400)	4.4 (0.8)	3.9 (0.7)

[a] Values in parentheses show the standard deviation.

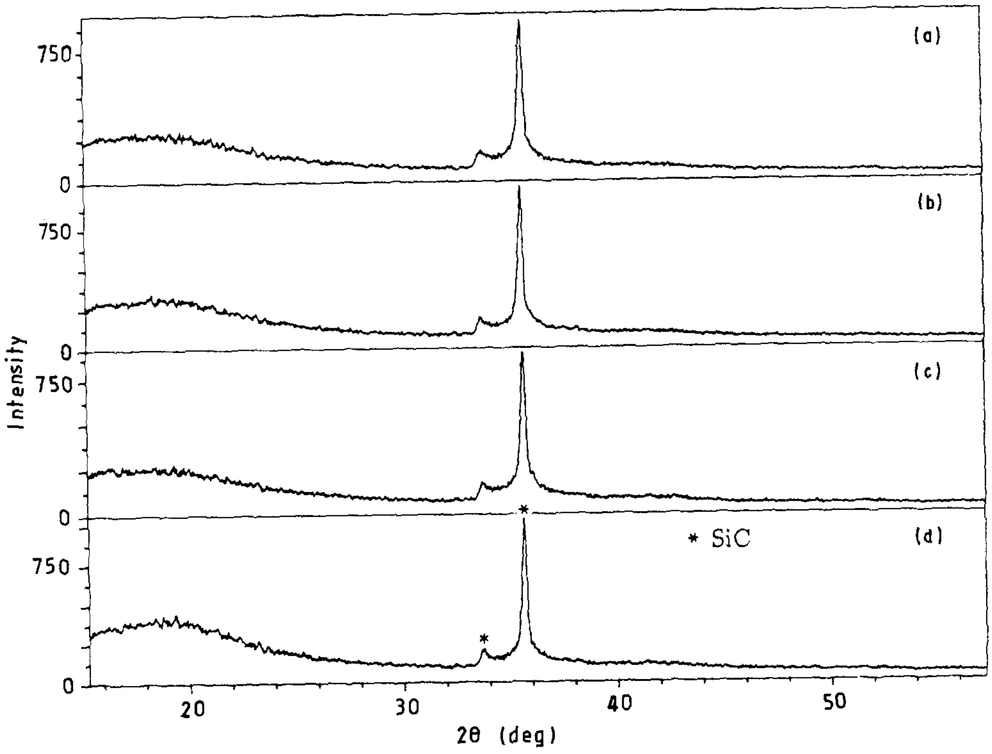

Figure 11 XRD patterns from four different points: from (a) the point at the cylindrical edge through two medium points (b and c) to (d) the centre, along the radius of the preform without any binder after heat treatment at 1100 °C in argon.

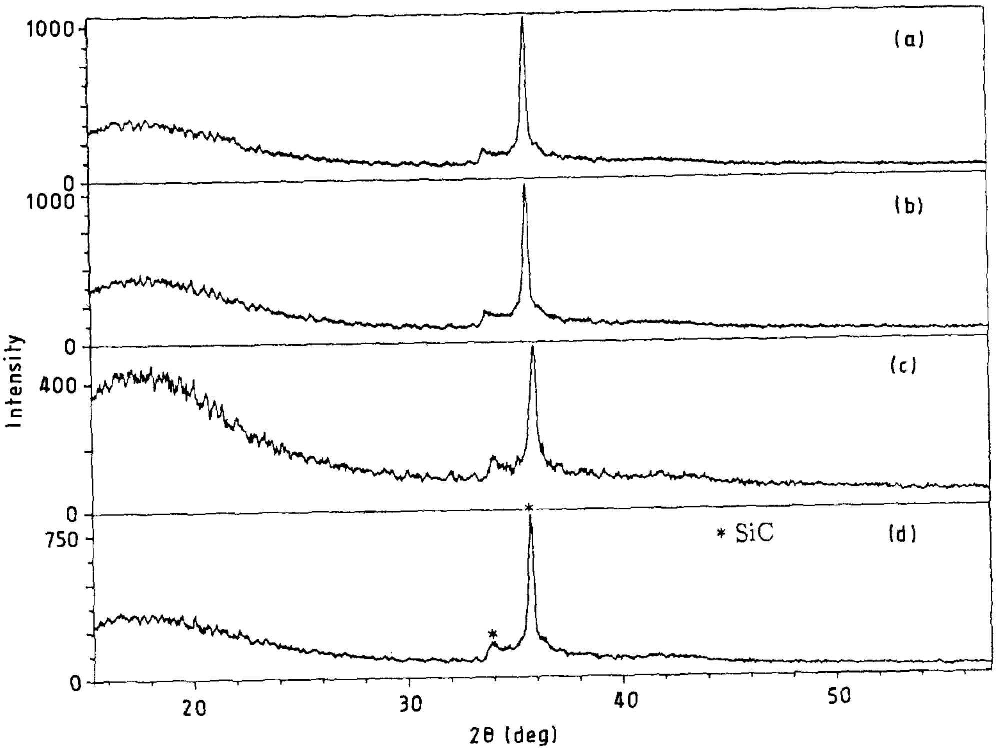

Figure 12 X-ray diffraction patterns from four different points: from (a) the point at the cylindrical edge through two medium points (b and c) to (d) the centre, along the radius of the preform without any binder after heat treatment at 1100 °C in air.

shows the XRD patterns from four different points along the radius of the preform. They also show no SiO_2 peak. This suggests that the formation of SiO_2 for the preform made with either binder required the presence of the binder. However, the weight uptake in Table II clearly shows that air greatly enhanced the formation of SiO_2 for both phosphate A23 and silica binders. Furthermore, more silica was formed near the preform surface for both silica (Fig. 4) and phosphate A23 (Fig. 8) binders. A possible reason for this in the case of the phosphate A23 binder is that the reaction between the binder and the SiC whiskers at 1100 °C damaged the whiskers, thereby enhancing the oxidation of the whiskers by oxygen in the air. This is supported by the fact that more binder was observed by SEM near the surface than at the centre of the preform made by using the phosphate A23 binder after heat treatment at 200 °C. For the case of the silica binder, the reason was probably that the impurity in the silica colloid (practical grade) accelerated the oxidation of the SiC whiskers by the oxygen in the air. The presence of sodium impurity was shown in the silica binder by energy-dispersive X-ray spectroscopy (Fig. 13, where the iron peaks are due to the SEM chamber rather than the sample and the carbon peak is due to the SEM sample holder). This is also supported by the fact that more binder was found near the surface than at the centre (Fig. 1a) of the preform made by using the silica binder after heat treatment at 200 °C.

An experiment was performed by immersing the SiC whisker preform in hydrofluoric acid (HF) for 4 days to dissolve away the SiO_2. Fig. 14 shows the scanning electron micrographs of the SiC whiskers from the surfaces of the preforms made using the silica and phosphate A23 binders after heat treatment at 1100 °C in air or in argon. For the sake of comparison, it also shows the plain SiC whiskers (without any binder) after the same HF treatment. The rough morphology of the whiskers in the etched preforms (1100 °C in air, i.e. Fig. 14a and c and the smooth morphology of the whiskers in the etched preform (1100 °C in argon, i.e. Fig. 14d) and in the etched SiC whiskers (without any binder, heated at 1100 °C in air, i.e. Fig. 14b) show that the SiO_2 formation was accompanied by significant whisker degradation only in the presence of both a binder and air.

Because the binder was mainly responsible for the formation of SiO_2, the SiO_2 distribution in the preform gave information on the distribution of the binder. Comparison of Figs 4 and 8 shows that the difference between the SiO_2 concentrations at the surface and the centre was much less for the phosphate binder than the silica binder, even though the contribution of SiO_2 from the silica binder itself in the preforms with the silica binder should have made the SiO_2 distribution more uniform in preforms with the silica binder. This means that the SiO_2 formed by whisker oxidation in air overshadowed the original SiO_2 from the silica binder.

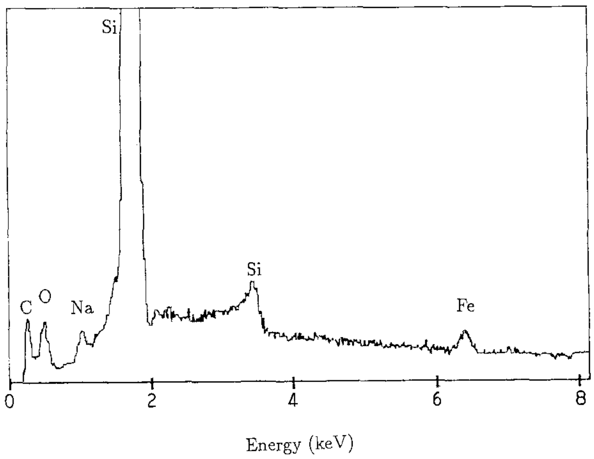

Figure 13 The presence of sodium impurity in the silica binder by energy dispersive X-ray spectroscopy.

4.4. Determining factors for strong preforms

The morphology, crystallinity and phase of a binder are probably among the factors which determine the binding ability of the binder. In addition, the reactivity between the binder and the whiskers is expected to enhance the binding ability. On the other hand, the strength of the bound material depends not only on the binding ability of the binder, but also on the amount of the binder used. This section assesses all these factors, with the objective of determining the major factors that govern the binding ability of the binder, which is related to the compressive strength of the preforms.

A study of the reaction between the SiC whiskers and the binders was performed by making blocks of SiC whiskers with the undiluted silica or phosphate solutions (without any water addition). This means that the binders were used at the concentration of one part of silica with zero parts of water or one part of the phosphate solution with zero parts of water. Although the absence of water was in contrast to the actual situation used in preparing a preform, it made the binder–whisker reaction experimentally more observable, as the binder concentration was higher in the SiC whisker blocks than in the whisker preforms.

After 200 °C drying for 3 days, the blocks were heat treated at 500, 800, 1100 °C (in air), 1100 and 1200 °C (in argon) for 4 h, as also performed in the preform preparation. For the sake of comparison, phosphoric acid, denoted A99, was also employed by itself as a binder to make a SiC whisker block. The SiC whisker block with phosphoric acid was dried at 200 °C for 3 days and then heat treated at 500 and 800 °C.

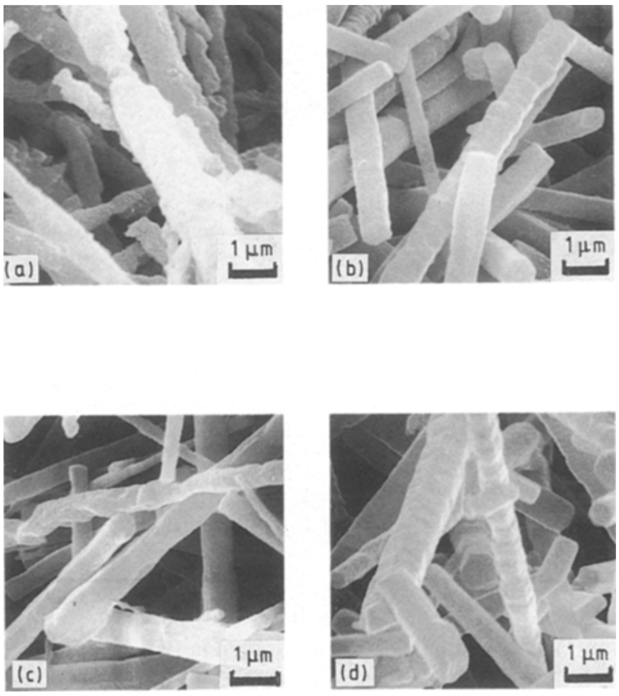

Figure 14 Scanning electron micrographs of the HF-treated SiC whiskers from the surfaces of the preforms made by using (a) the phosphate A23 binder after heat treatment at 1100 °C in air, (b) without any binder, (c) the silica binder at 1100 °C in air, and (d) the silica binder at 1100 °C in argon.

The XRD patterns of the block make by using the undiluted silica solution are shown in Fig. 15. The SiC whisker block underwent no apparent reaction when it was heat treated at 800 °C or less. A small amount of SiO_2 (probably a combination of tridymite and cristobalite) was formed after heat treatment at 1100 °C in argon. When the SiC whisker block was heat treated at 1100 °C in air, the SiO_2/SiC intensity ratio was much higher. This might be due to the SiC whiskers being consumed by the vast oxidation through the supply of oxygen from the air. A large amount of cristobalite SiO_2 was formed after heat treatment of 1200 °C in argon.

Fig. 16 shows the XRD patterns of the whisker block made by using the undiluted phosphate A03 solution after heat treatment at 500, 800, 1100 °C (in air) and 1200 °C (in argon). No reaction product was observed for the SiC whisker block after heat treatment at 500 °C. When the SiC whisker block was heat treated at 800 °C, the reaction product was probably tridymite SiO_2 together with a large amount of type A aluminium metaphosphate ($Al(PO_3)_3(A)$).

The relative reactivity between the phosphate binder and the SiC whisker was obtained by summing the relative reactivities of all associated reaction products. The relative reactivity of each reaction product was measured by dividing the sum of the peak intensities of all XRD peaks from that reaction product by the sum of the peak intensities of all peaks from the SiC whiskers. The relative binder amount was also obtained by summing the contributions from all binder phases, such that the relative amount of each phase was measured by dividing the sum of the intensities of all XRD peaks from that phase by the sum of the intensities of all peaks from the SiC whiskers. This gives relative reactivities of 0 and 2.9 and relative binder amounts of 62.3 and 28.3 for the SiC whisker blocks after heat treatment at 500 and 800 °C, respectively.

Fig. 16 also shows the complete consumption of the SiC whiskers with the presence of a small amount of type A aluminium metaphosphate ($Al(PO_3)_3$) for the SiC whisker block after heat treatment at 1100 °C in air. It is probable that much more amorphous phase

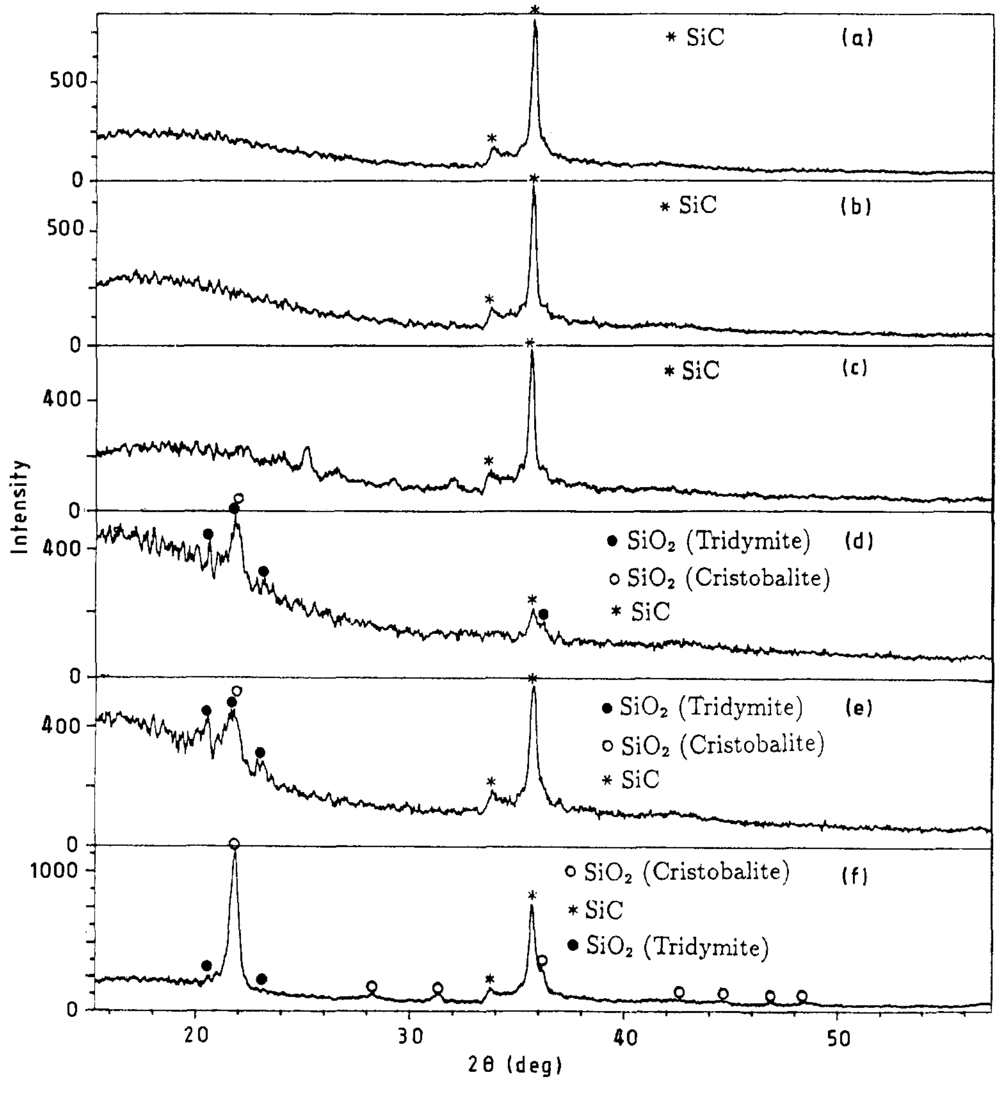

Figure 15 XRD patterns of the SiC whisker block with the undiluted silica binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air), (e) 1100 and (f) 1200 °C (in argon).

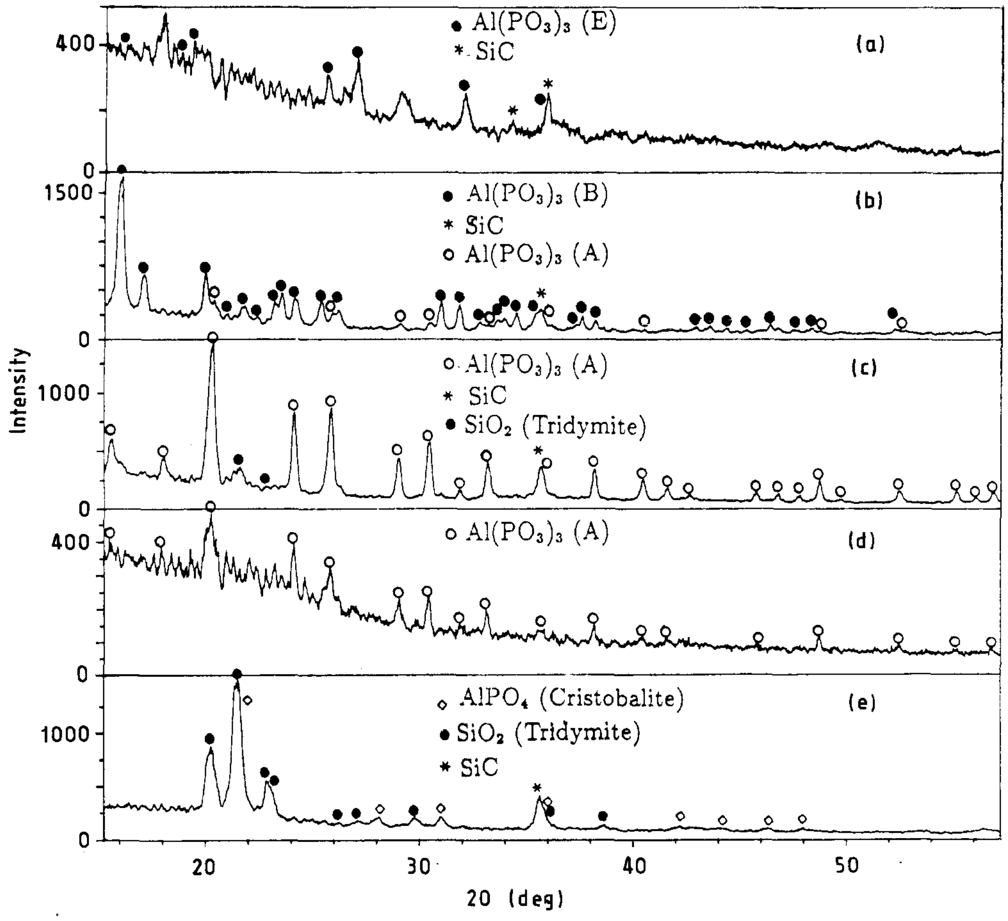

Figure 16 XRD patterns of the SiC whisker block with the undiluted phosphate A03 binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air) and (e) 1200 °C (in argon).

than crystalline phase exists because the final product after heating was almost transparent and the intensity was quite low for all the XRD peaks. The relative reactivity is denoted as infinity (∞) in this case because no SiC whisker remained.

When the SiC whisker block was heat treated at 1200 °C in argon, a large amount of tridymite SiO_2 was formed together with a small amount of cristobalite $AlPO_4$. The relative reactivity was 20.3 and the relative amount of the binder was 7.1 for the SiC whisker block heat treated at 1200 °C in argon.

XRD patterns of the SiC whisker block made by using the undiluted phosphate A06 solution after heat treatment at 500, 800, 1100 °C (in air), 1100 and 1200 °C (in argon) are shown in Fig. 17. The use of undiluted phosphate A06 solution resulted in a medium reactivity between the binder and the SiC whiskers. The reaction product for the SiC whisker block after heat treatment at 500 °C was identified as two forms of silicon phosphate (both SiP_2O_7, with different arrangement of Si^{4+} and $P_2O_7^{4-}$), together with a larger amount of crystalline materials, which was mostly type B aluminium metaphosphate, and a small amount of type A aluminium metaphosphate. Its reactivity was 11.3, which was higher than that of the SiC whisker block made with the phosphate A03 solution. The relative amount of the binder was calculated as 34.1. The relative reactivity became even higher when the SiC whisker block was heat treated at 800 °C. The reaction products were again the two forms of silicon phosphate (SiP_2O_7). The crystalline binder formed after this heating was only type A $Al(PO_3)_3$. The reactivity was increased to 15.1 and the relative amount of the binder was 20.8. When the SiC whisker block was heat treated at 1100 and 1200 °C in argon, tridymite SiO_2 was formed. The amount of SiO_2 was less than that of the SiC whisker block made by using the phosphate A03 solution after heat treatment at 1200 °C in argon. The relative reactivities were 7.7 and 9.7 for heat treatments at 1100 and 1200 °C in argon, respectively. The binder phases were an amorphous phase and cristobalite $AlPO_4$ for heat treatments at 1100 and 1200 °C in argon, respectively. The relative amount of the binder was 2.6 for the SiC whisker block heat treated at 1200 °C in argon, but could not be determined for that heat treated at 1100 °C in argon due to the binder's amorphous structure. A very strong reaction was found for the block heat treated at 1100 °C in air. In this case, all the SiC whiskers were consumed through the reaction together with a glassy phase and a small amount of type A $Al(PO_3)_3$. Again, the reactivity was infinity.

Fig. 18 shows the XRD patterns of the SiC whisker block made by using the undiluted phosphate A12 solution after heat treatments at 500, 800, 1100 °C (in air) and 1100 °C (in argon). When the SiC whisker block was heat treated at 500 °C, silicon phosphate (SiP_2O_7) was formed again in two forms, together with

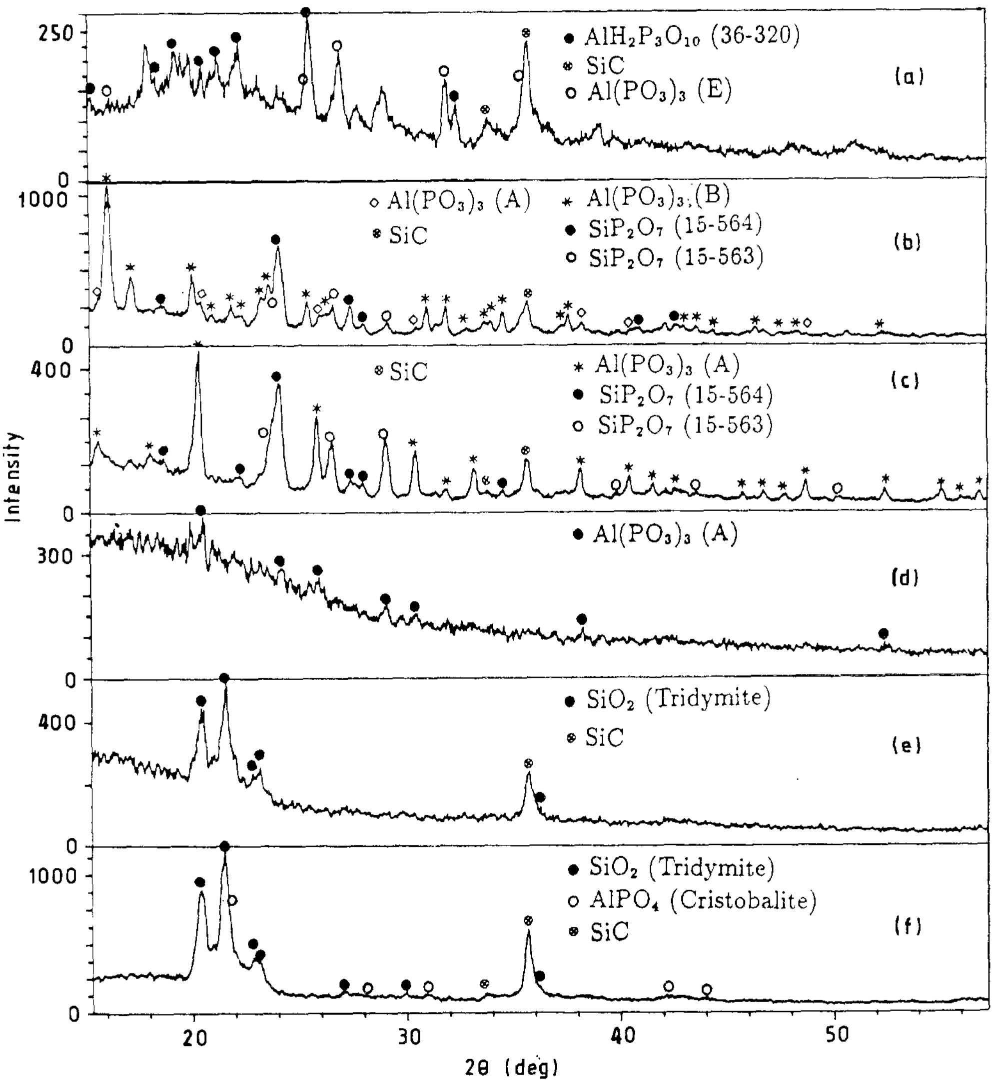

Figure 17 XRD patterns of the SiC whisker block with the undiluted phosphate A06 binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air), (e) 1100 and (f) 1200 °C (in argon).

the binder phases which were types A and B $Al(PO_3)_3$. The relative reactivity was 12.0 and the relative binder amount was 16.1 for this SiC whisker block. More silicon phosphate was formed when the SiC whisker block was heat treated at 800 °C. Similar to that of the case of the phosphate A06 binder, the remaining binder was only type A $Al(PO_3)_3$. The relative reactivity and relative amount of the binder were 17.7 and 15.7, respectively. The formation of tridymite SiO_2 led to a reactivity of 4.9 for the SiC whisker block after heat treatment at 1100 °C in argon. Again, similar to the case of the phosphate A06 solution, the SiC whisker block heat treated at 1100 °C in air had a strong reaction, which led to a reactivity of infinity.

Fig. 19 shows the XRD patterns of the SiC whisker block made by using the undiluted phosphate A23 solution after heat treatment at 200, 500, 800, 1100 °C (in air), 1100 and 1200 °C (in argon). It shows that no reaction product was formed for the one heat treated at 200 °C. The reaction produced the two forms of silicon phosphate for the SiC whisker block heat treated at 500 or 800 °C. The relative reactivities were 14.1 and 18.9 for heat treatments at 500 or 800 °C, respectively. The binder phase found for these two blocks was type A $Al(PO_3)_3$. The relative amounts of the binder were 5.7 and 5.0 when heat treated at 500 and 800 °C, respectively. The formation of a small amount of reaction product (tridymite SiO_2) means less reactivity, namely 2.3 and 2.5, for the SiC whisker block after heat treatment at 1100 and 1200 °C in argon, respectively. These values are much smaller compared to those of the SiC whisker blocks made by using the undiluted phosphate A03 and A06 solutions. The binder phase present in the SiC whisker block after these two heat treatments is believed to be a glassy phase for either case. The relative reactivity was also infinity for the block after heat treatment at 1100 °C in air.

XRD patterns of the SiC whisker block made by using the undiluted phosphate MAP solution after heat treatment at 500, 800, 1100 °C (in air), 1100 and 1200 °C (in argon) are shown in Fig. 20. No reaction product was found for the SiC whisker block after heat treatment at 500 °C. The binder phases found were the types A and B $Al(PO_3)_3$. The relative amount of the binder was 29.2. At 800 °C, a minor amount of silicon phosphate (SiP_2O_7) was formed, together with a large amount of binder phases, again types A and B

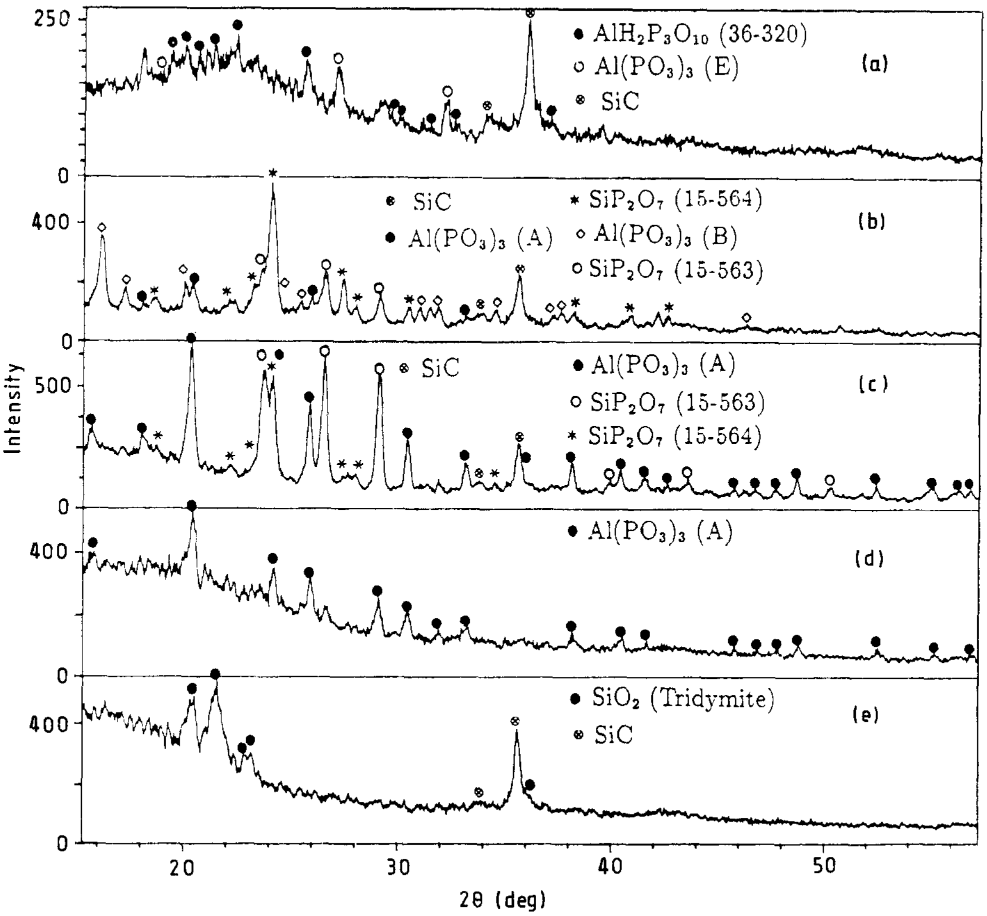

Figure 18 XRD patterns of the SiC whisker block with the undiluted phosphate A12 binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air) and (e) 1100 °C (in argon).

of $Al(PO_3)_3$. Its relative reactivity was 4.5 and the relative binder amount was 26.8. When the SiC whisker block was heat treated at 1100 °C in argon, only a small amount of tridymite SiO_2 was formed. Its relative reactivity was 2.9. When it was heat treated at 1200 °C in argon, much more tridymite SiO_2 was formed. The relative reactivity became 10.3, which was comparable to that with phosphate A03 and A06 solutions. Strong reaction was also found for the SiC whisker block after heat treatment at 1100 °C in air. All the SiC whiskers were consumed in this case too.

Fig. 21 shows the XRD patterns of the SiC whisker block made by using phosphoric acid (A99) after heat treatment at 200, 500 and 800 °C. It showed that no reaction product was found after drying at 200 °C. Two types of silicon phosphate were observed after heat treatment at 500 or 800 °C. The relative reactivities were 30.6 and 46.9 for 500 and 800 °C, respectively.

TABLE VIII Smoothness and porosity of the phosphate binders

Heat-treatment temperature (°C)	A03	A06	A12	A23	MAP
200					
500	s L	s M	m M	m H	s H
800	m L	m M	m M	r H	m H
1100 (air)				s H	
1100 (argon)					
1200 (argon)	s M			s L	s H

Roughness: s, smooth; m, medium; r, rough.
Porosity: H, high; M, medium; L, low.

Effort was made to correlate the compressive strength of the preform with several parameters, such as the morphology and phase of the binder, the phase of the binder in the presence of the SiC whiskers and the reactivity of the phosphate binder solution with the SiC whiskers. The roughness and porosity of the phosphate binders after heat treatments, described in Part I [1], are listed in Table VIII. When the binders were heat treated at 500 or 800 °C, the porosity increased as the P/Al atom ratio increased from 3 to 23. The only exception was the phosphate MAP binder, which contained about 40% water as received from the manufacturer. This water content would make the porosity higher upon heating. The roughness of the binders after the same heat treatments also increased as the atom ratio increased from 3 to 23, and increased as the heat-treatment temperature increased from 500 °C to 800 °C for the same binder. When the binder solutions were heat treated at 1200 °C in argon, the crystalline phase decomposed to form aluminium metaphosphate or transformed to the metaphosphate

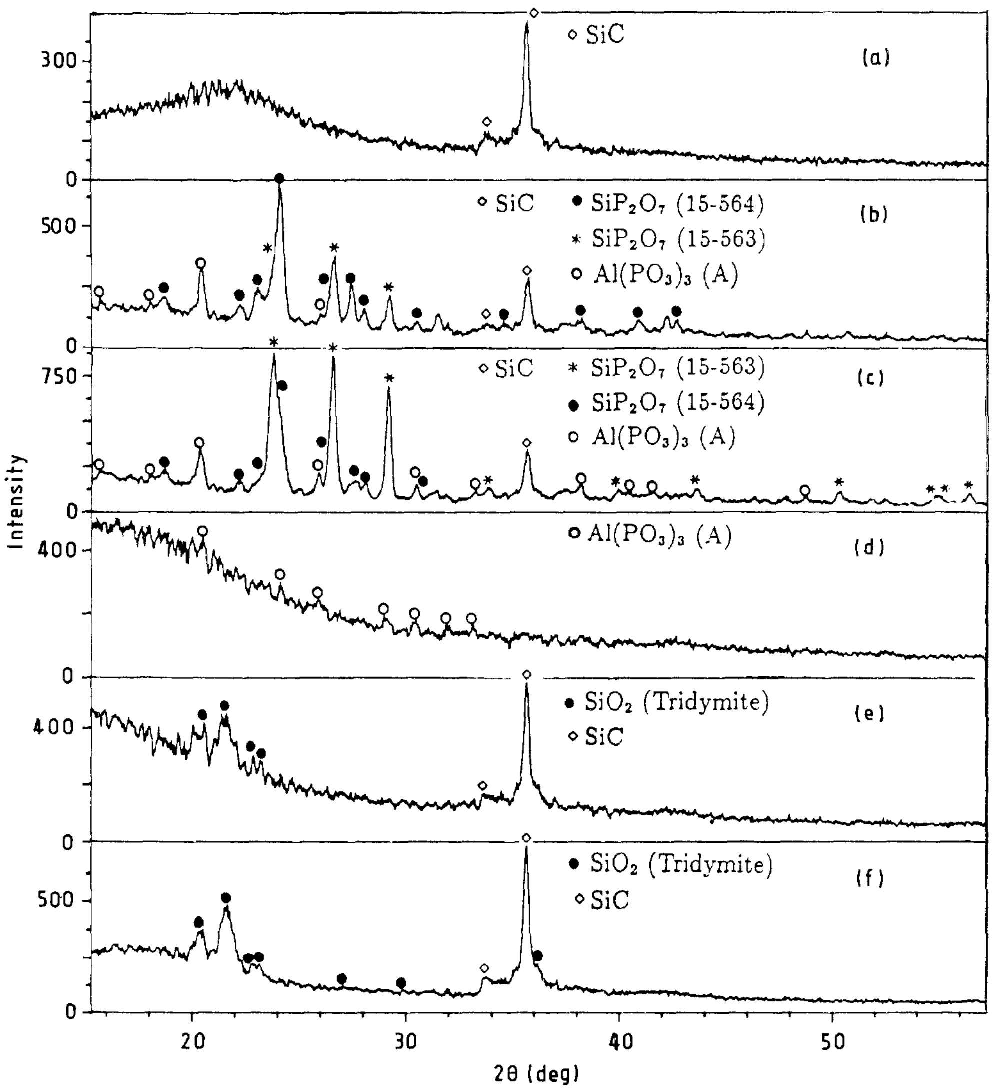

Figure 19 XRD patterns of the SiC whisker block with the undiluted phosphate A23 binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air), (e) 1100 and (f) 1200 °C (in argon).

glass. The formation of a glassy phase led the phosphate A23 binder to a low porosity. The decomposition of aluminium metaphosphate to aluminium orthophosphate increased the porosity of the phosphate A03 binder while the phosphate MAP binder remained high in porosity. All three binders (phosphates A03, A23 and MAP) locally showed smooth morphology under this heat treatment condition (1200 °C in argon).

Table IX shows the crystalline phases of the binders, also described in Part I [1], after the same heat treatments. The phosphate A03 and MAP binders formed different types of aluminium hydrogen phosphate after drying at 200 °C. However, the phosphate A23 binder was amorphous after the same drying treatment. It was found that when the atom ratio approached 3, type B aluminium metaphosphate ($Al(PO_3)_3$) always formed when the phosphate solutions were heat treated at 500 °C. As the atom ratio increased, type A aluminium metaphosphate ($Al(PO_3)_3$) began to form. When the heating temperature was increased, type B aluminium metaphosphate ($Al(PO_3)_3$) tended to transform to type A aluminium metaphosphate ($Al(PO_3)_3$) [4]. The phosphate A23 binder changed to form the metaphosphate glass after heat treatment at 1100 °C in air. It formed the metaphosphate glass together with some aluminium orthophosphate ($AlPO_4$) when heat treated at 1200 °C in argon. At 1200 °C in argon, both the phosphate A03 and MAP binders decomposed to form $AlPO_4$.

The relative reactivities and the relative amounts of the binders (*ex situ*) are summarized in Table X. For each combination of binder composition and heat-treatment temperature, this table shows, from top to bottom of each box, (i) the phase(s) of the reaction product(s) and their relative reactivities (together with the sum, S_r, of the reactivities for all reaction products), and (ii) the binder phase(s) and their relative amounts (together with the sum, S_b, of the relative amounts of all binder phases). The reactivity sum, S_r, increased as the heat-treatment temperature increased from 500 °C to 800 °C to 1100 °C (in air) for all the phosphate binder cases. The relative reactivity also increased when the heat treatment condition went from 500 °C to 800 °C to 1200 °C (in argon) for the phosphate A03 binder case. However, the relative

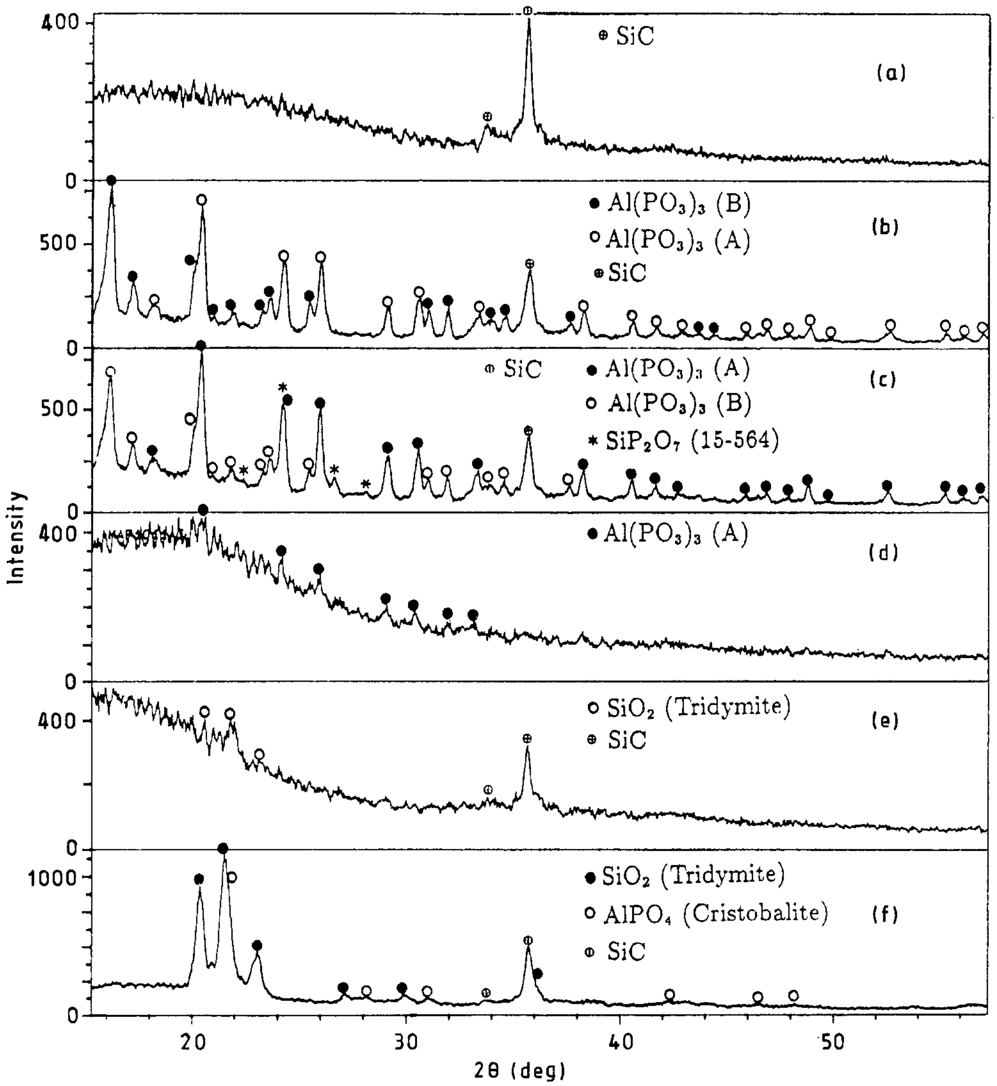

Figure 20 XRD patterns of the SiC whisker block with the undiluted phosphate MAP binder after heat treatment at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air), (e) 1100 and (f) 1200 °C (in argon).

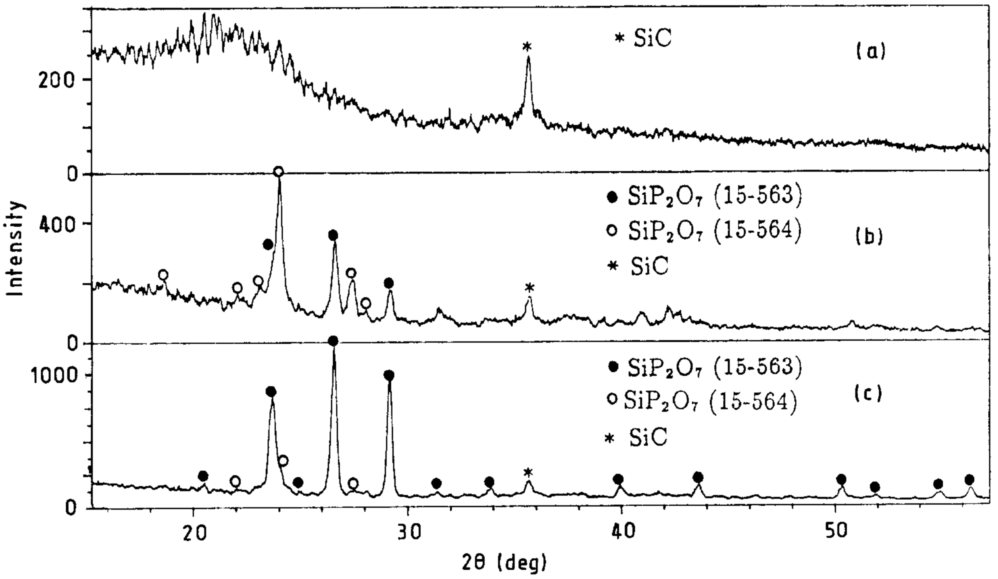

Figure 21 XRD patterns of the SiC whisker block made by using the phosphoric acid (A99) after heat treatment at (a) 200, (b) 500 and (c) 800 °C.

reactivity was lower when the heat treatment was performed at 1100 or 1200 °C in argon for the phosphate binders A06, A23 and MAP.

Comparison of the phosphate binders A03, A06, A12 and A23 shows that the reactivity sum, S_r, increased monotonically as the P/Al atom ratio increased from 3 to 23 when the SiC whisker block was heat treated at both 500 and 800 °C. However, the change of S_r as the P/Al atom ratio increased from 3 to 6 was larger than that of S_r as the P/Al atom ratio increased from 6 to 23. This trend may be due to the contribution of the extra phosphoric acid from the phosphate solutions A06, A12 and A23. Phosphoric acid was reported by Kingery [5] to react with siliceous materials to form silicon phosphate (SiP_2O_7). It was also confirmed by the result of the SiC whisker block made by using the phosphoric acid (A99), which showed that the silicon phosphates were formed after heating at 500 and 800 °C. Phosphoric acid (A99) showed the highest relative reactivity among the phosphate binders. However, it cannot be used as a binder to make a SiC whisker preform because it cannot retain the shape below 500 °C. The reason for not comparing the phosphate solution MAP with other binders is because this solution had 40% water when received. Generally, the relative reactivity and the relative amount of binder was lower for the SiC whisker block made with the phosphate solution

TABLE IX Crystalline phase of the phosphate binders

Heat-treatment temperature (°C)	A03	A06	A12	A23	MAP
200	C	–	–	M	H
500	B	A	A	A	B
800	B + A	A	A	A	B + A
1100 (air)	–	–	–	G	–
1100 (argon)	–	–	–	–	–
1200 (argon)	P	–	–	G + P	P

M, amorphous; A, aluminium metaphosphate $Al(PO_3)_3$(A); B, aluminium metaphosphate $Al(PO_3)_3$(B); G, metaphosphate glass; P, aluminium orthophosphate $AlPO_4$ (cristobalite); H, aluminium hydrogen phosphate $AlH_2P_3O_{10}$; C, aluminium hydrogen phosphate $Al(H_2PO_4)_3$(C).

TABLE X The relative reactivity and the relative amount of the binder in the presence of the SiC whiskers

Heat-treatment temperature (°C)	A03	A06	A12	A23	MAP	A99
200	0	0	0	0	0	0
	[E]	[H]	[H]	[M]	[M]	
		[E]	[E]			
500		(Z): 7.7 (0.2)	(Z): 8.0 (0.1)	(Z): 8.7 (0.1)		(Z): 16.8 (0.4)
		(Y): 3.6 (0.1)	(Y): 4.0 (0.1)	(Y): 5.4 (0.1)		(Y): 13.8 (0.4)
		S_r: 11.3 (0.2)	S_r: 12.0 (0.1)	S_r: 14.1 (0.1)		S_r: 30.6 (0.6)
	[A]: 5.7 (0.2)	[A]: 3.8 (0.1)	[A]: 3.8 (0.1)	[A]: 5.7 (0.1)	[A]: 12.0 (0.2)	
	[B]: 56.6 (2.4)	[B]: 30.3 (0.8)	[B]: 12.3 (0.2)		[B]: 17.2 (0.3)	
	S_b: 62.3 (2.4)	S_b: 34.1 (0.8)	S_b: 16.1 (0.2)	S_b: 5.7 (0.1)	S_b: 29.2 (0.4)	
800	(T): 2.9 (0.1)	(Z): 8.0 (0.2)	(Z): 6.1 (0.1)	(Z): 6.4 (0.1)	(Z): 4.5 (0.1)	(Z): 5.4 (0.1)
		(Y): 7.1 (0.2)	(Y): 11.6 (0.2)	(Y): 12.5 (0.2)		(Y): 41.5 (1.1)
	S_r: 2.9 (0.1)	S_r: 15.1 (0.3)	S_r: 17.7 (0.2)	S_r: 18.9 (0.2)	S_r: 4.5 (0.1)	S_r: 46.9 (1.1)
	[A]: 28.3 (0.8)	[A]: 20.8 (0.5)	[A]: 15.7 (0.3)	[A]: 5.0 (0.1)	[A]: 14.5 (0.2)	
					[B]: 12.3 (0.2)	
	S_b: 28.3 (0.8)	S_b: 20.8 (0.5)	S_b: 15.7 (0.3)	S_b: 5.0 (0.1)	S_b: 26.8 (0.3)	
1100 (air)	∞	∞	∞	∞	∞	–
			(3)			–
						–
	[G]	[G]	[G]	[G]	[G]	–
	[A]	[A]	[A]	[A]	[A]	–
						–
1100 argon)	–	(T): 7.7 (0.1)	(T): 4.9 (0.0)	(T): 2.3 (0.0)	(T): 2.9 (0.0)	–
	–					–
	–	S_r: 7.7 (0.1)	S_r: 4.9 (0.0)	S_r: 2.3 (0.0)	S_r: 2.9 (0.0)	–
	–	[G]	[G]	[G]	[G]	–
	–					–
	–					–
1200 (argon)	(T): 20.3 (0.6)	(T): 9.7 (0.1)	–	(T): 2.5 (0.0)	(T): 10.3 (0.2)	–
			–			–
	S_r: 20.3 (0.6)	S_r: 9.7 (0.1)	–	S_r: 2.5 (0.0)	S_r: 10.3 (0.2)	–
	[P]: 7.1 (0.2)	[P]: 2.6 (0.0)	–	[G]	[P]: 4.0 (0.1)	–
			–			–
	S_b: 7.1 (0.2)	S_b: 2.6 (0.0)	–		S_b: 4.0 (0.1)	–

Reaction products: (Z), silicon phosphate SiP_2O_7(15-564); (Y), silicon phosphate SiP_2O_7(15-563); (T), tridymite SiO_2; S_r, summation of relative reactivity.

Binder phases: [A], aluminium metaphosphate $Al(PO_3)_3$(A); [B], aluminium metaphosphate $Al(PO_3)_3$(B); [P], cristobalite aluminium orthophosphate $AlPO_4$; [G], metaphosphate glass; [M], amorphous; [D], aluminium metaphosphate $Al(PO_3)_3$(D); [E], aluminium metaphosphate $Al(PO_3)_3$(E); [H], aluminium hydrogen phosphate $AlH_2P_3O_{10}$; S_b, summation of relative *ex situ* binder amount.

MAP than that with the phosphate solution A03 for both 500 and 800 °C heat treatments, even though both MAP and A03 have the P/Al atom ratio equal to 3. This is probably due to the 40% water in the phosphate solution MAP.

The trend of the reactivity sum, S_r, versus the P/Al atom ratio for the SiC whisker block after heat treatment at 500 and 800 °C was opposite that of the SiC whisker block heat treated at 1100 and 1200 °C in argon. The reactivity sum, S_r, decreased as the P/Al atom ratio increased from 3 to 23 for 1100 or 1200 °C, probably because the effective binder amount was larger for the phosphate binder with a lower value of the P/Al atom ratio. When the SiC whisker block was heat treated in argon, the extra phosphoric acid might be driven out by the flowing argon. The higher the P/Al atom ratio, the greater is the phosphoric acid content. Therefore, the higher the P/Al atom ratio, the less is the effective binder remaining when heated up to 1100 or 1200 °C in argon. The lower the effective binder content, the less is the chance of forming SiO_2.

The results discussed above, together with the phosphoric acid content from Table III of Part I [1], are further summarized in Table XI. This table shows in each box, from the top line to the bottom line of the box, the following information: (i) the phase(s) of the phosphate binders by themselves and the binder roughness and porosity, (ii) the phosphoric acid amount, (iii) the phase(s) of the binders in the presence of the SiC whiskers, together with the relative amount of the binder, and (iv) the reaction product phase, together with the relative reactivity between the binder and the whiskers. The acid phosphoric amount in (ii) was obtained from Table III of Part I [1] by calculating the difference of the P/Al atom ratio between 500 and 800 °C. From Table XI (the first line and third line in each box), it was found that the presence of the SiC whiskers modified the chance of forming a pure type B aluminium metaphosphate $Al(PO_3)_3$ for the cases with the phosphate A03 and MAP binders. The consequence was a combination of types B and A $Al(PO_3)_3$. Similarly, the phosphate A06 and A12 binders yielded combinations of types B and A $Al(PO_3)_3$ in the presence of the SiC whiskers.

Table XII combines Tables IV and V and shows the compressive strength of the preforms made by using the phosphate binders after heat treatment at various temperatures and in various environments. Effort was made by comparing Tables XI and XII to extract the major factors that make the preform strong. In comparing the cases of SiC whisker preforms made by using the phosphate A03, A06, A12 and A23 binders after heat treatment at 500 °C, it was found that the relative amount of binder played an important role. The preform made by using the phosphate A03 binder had a vast amount of binder (Table XI). This led it to be the strongest one of these four, although it had no detectable binder–whisker reaction. The preform

TABLE XI Summary of the parameters for the phosphate binders and the reaction product

Heat-treatment temperature (°C)	A03		A06		A12		A23		MAP		A99	
200												
							M					
								0				
500	B	sL	A	sM	A	mM	A	mH	B	sH		
	PA	5	PA	12			PA	19				
	B + A	62.3	B + A	34.1	B + A	16.1	A	5.7	B + A	29.2		
		0	SP	11.3	SP	12.0	SP	14.1	SP	0	SP	40.6
800	B + A	mL	A	mM	A	mM	A	rH	B + A	mH		
	A	28.3	A	20.8	A	15.7	A	5.0	A + B	26.8		
	T	2.9	SP	15.1	SP	17.7	SP	18.9	SP	4.5	SP	46.9
1100 (air)							G	sH				
							G + A					
								∞				
1100 (argon)												
							G					
							T	2.3				
1200 (argon)	P	sH					G + P	sL	P	sH		
	P	7.1					G	$\leqslant 5.0$	P	4.0		
	T	20.3					T	2.5	T	10.3		

M, amorphous; A, aluminium metaphosphate $Al(PO_3)_3$(A); B, aluminium metaphosphate $Al(PO_3)_3$(B); G, metaphosphate glass; P, aluminium orthophosphate $AlPO_4$ (cristobalite); T, tridymite SiO_2; SP, silicon phosphate (SiP_2O_7); PA, phosphoric acid (H_3PO_4).
Roughness: s, smooth; m, medium; r, rough.
Porosity: L, low; M, medium; H, high.

TABLE XII Summary of the compressive strength of the SiC whisker preforms made by using the phosphate binders

Heat-treatment temperature (°C)	A03	A06	A12	A23	MAP
200				1.64 (0.13)[a]	
500	9.08 (0.23)	6.25 (0.23)	6.11 (0.18)	5.93 (0.20)	6.75 (0.55)
800	11.98 (0.49)	11.67 (0.17)	11.53 (0.29)	11.04 (0.20)	
1100 (air)				15.90 (0.15)	
1100 (argon)				7.44 (0.24)	
1200 (argon)	10.52 (0.31)			7.99 (0.42)	9.28 (0.27)

[a] Values in parentheses show the standard deviation.

made by using the phosphate A23 binder had a stronger binder–whisker reaction, which compensated for its small amount of binder, thereby resulting in a slightly lower compressive strength compared to that with the phosphate A06 and A12 binders, which had higher binder amounts and lower relative reactivities, after heat treatment at the same temperature.

When comparing the preforms after heat treatment at 800 °C, the relative binder amount of the preform made by using the phosphate A03 binder was the largest (but not much larger than the preform made by using the phosphate A06, A12 or A23 binders). However, the relative reactivity was smallest for the preform made by using the phosphate A03 binder. Hence, the preform made by using the phosphate A03 binder had a similar compressive strength to those of the preforms made by using the phosphate A06, A12 and A23 binders. The amount of phosphoric acid for the phosphate A03, A06 and A23 binders exhibited a similar trend as S_r of the preform under the same heat-treatment conditions. This clearly demonstrates that S_r was mainly governed by the amount of the extra phosphoric acid. The binder with smoothness and low porosity might have enhanced the compressive strength of the preform made by using the phosphate A03 binder at 500 °C, though it had no apparent binder–whisker reaction.

The binder amount shown in Table XI for the SiC whisker block made by using the phosphate A23 binder at 1200 °C (in argon) was smaller than 5.0. This was determined by noting that the binder amount in the preform heat treated at a higher temperature (1200 °C) could not be larger than that in the preform heat treated at a lower temperature (800 °C).

When comparing the SiC whisker preforms made by using the phosphate A03 and A23 binders after heat treatment at 1200 °C in argon, both S_b and S_r are higher for the preform with the phosphate A03 binder. This leads to a higher compressive strength for the preform with the phosphate A03 binder. However, the effect of the binder phases is not clear in this case.

Among the SiC whisker preforms made by using the phosphate A23 binder after heat treatment at 200, 500, 800 and 1100 °C (in air) the large variation of S_r, rather than the small variation of S_b, played an important role: the larger S_r, the stronger was the preform. According to Kingery [5], phosphoric acid attacks the silicate portion and probably helps the bonding action. (Silicon carbide is also called carbon silicate). As the reactivity increased with increasing temperature, this trend is consistent with the notion of Kingery.

In comparing SiC whisker preforms made by using the phosphate A23 binder after heat treatment at 500 and 1200 °C (in argon), it was found that the metaphosphate glass (at 1200 °C in argon), having a smooth morphology and a low porosity, was more effective than type A aluminium metaphosphate in strengthening the preform, even though its value of S_r was only 2.5 compared to a value of 14.1 at 500 °C. This indicates that the metaphosphate glass could have been a superior binder if S_r were maintained somehow.

In comparing the SiC whisker preforms made by using the phosphate A03 binder after heat treatment at 500, 800 and 1200 °C (in argon), it was found that S_r increased and S_b decreased as the heating temperature increased. Because both quantities changed by large amounts, the effect of the binder phase or morphology, if any, is not clear.

In conclusion, the determining parameters for the compressive strength of the preforms are S_r and S_b. The binder phase and morphology are less important. Comparison of the preforms made with the same binder after heat treatment at 200, 500 and 1100 °C (in air) showed that S_r played an important role because S_b did not vary much. However, comparison of the preforms made with the same binder after heat treatment at 500, 800 and 1100 °C (in argon) and 1200 °C (in argon) showed that the binder phase and morphology also played certain roles. The value of S_r generally increased with increasing temperature if the binder and heating environment were fixed. Comparison of the preforms made with different binders after heat treatment at the same temperature showed that S_b played a more important role than S_r, because the variation of S_r was relatively small.

4.5. *Ex situ* and *in situ* binders for SiC whiskers

The reaction product, such as silicon phosphate (SiP_2O_7) or tridymite SiO_2, which strengthened the compressive strength of the SiC whisker preform, acted as a binder produced *in situ*. Therefore, the reaction product is also called an *in situ* binder in this study. In contrast, the binder actually applied for making the preforms, such as silica or phosphates, is called an *ex situ* binder. Table XIII shows the *ex situ* and *in situ* binders for SiC whiskers. The term S_b refers to that from the *ex situ* binder only. The term S_r refers to the amount of reaction products, which serve as *in situ* binders.

The formation of the *in situ* binder for the SiC whisker preform resulted in strengthening due to

TABLE XIII *Ex situ* and *in situ* binders for SiC whiskers

	Ex situ	*In situ*
Silica binder[a]	SiO_2 (glass)	None
Silica binder[b]	SiO_2(C)	SiO_2(C)
Phosphate A03 binder	$Al(PO_3)_3$(A + B)	AlP
Phosphate A06 binder	$Al(PO_3)_3$(A + B)	SiP_2O_7, AlP
Phosphate A12 binder	$Al(PO_3)_3$(A + B)	SiP_2O_7, AlP
Phosphate A23 binder[a]	$Al(PO_3)_3$(A)	SiP_2O_7, AlP
Phosphate A23 binder[b]	$Al(PO_3)_3$(A) + G	SiO_2(C), AlP
Phosphate A23 binder[c]	G	SiO_2(T), AlP

[a] Heated < 1100 °C in air.

[b] Heated ≥ 1100 °C in air.

[c] Heated ≥ 1100 °C in argon.

C, cristobalite SiO_2; T, tridymite SiO_2; G, metaphosphate glass.

chemical reaction bonding. The increase of the compressive strength of the SiC whisker preforms is desirable for near net-shape casting.

TABLE XIV Compressive strength of carbon fibre preforms

Binder	Treatment temperature (°C)	Compressive strength (kPa)	Volume fraction (%)
Silica	200	200	60
	800	360	57
	1100	80	60
Phosphate A23 (1:15 water)	200	2390	57
	800	1630	57
	1100	40	53
Water glass	200	560	55
	800	1150	57
	1000	320	50
Acrylic emulsion	200	1870	53
	800	80	53
	1100	40	57
Phosphate A23			
(1:15 acetone)	200	2410	54
(1:5 acetone)	200	2120	55

5. Carbon fibre preform characterization

5.1. Compression testing

Compression testing was performed on the carbon fibre preforms to determine the binding ability of the binders used. Table XIV shows the compressive strengths of the carbon fibre preforms made by using the silica, phosphate A23, water glass and acrylic emulsion binders. The preforms made by using the silica and water glass binders had the highest compressive strength after heat treatment at 800 °C in argon, the second highest at 200 °C and the lowest at 1100 or 1000 °C in argon. The preforms made by using the water glass binder had higher compressive strengths than those made by using the silica binder for similar heat-treatment temperatures. On the other hand, the carbon fibre preforms made by using the phosphate A23 (water) and acrylic emulsion binders had the highest compressive strength after heat treatment at 200 °C. Their compressive strengths decreased as the heat-treatment temperature increased from 200 °C to 800 °C (in argon), and to 1100 °C (in argon).

The compressive strength of the carbon fibre preform made by using the phosphate A23 binder with the binder/acetone ratio of $\frac{1}{15}$ was similar to that of the preform made by using the phosphate A23 binder/water ratio of $\frac{1}{15}$. On the other hand, the compressive strength of the carbon fibre preform made by using the phosphate A23 binder with the binder/acetone ratio of $\frac{1}{5}$ after drying at 200 °C was slightly lower than that of the preform made with the binder/water or binder/acetone ratio of $\frac{1}{15}$ after the same drying treatment, even though the binder amount was much larger in the former (Table III). The reason is that the preform made with acetone was not totally dry after even 1 week of heating at 200 °C, whereas that made with water ($\frac{1}{15}$) or acetone ($\frac{1}{15}$) was totally dry after this drying treatment. The preform made with acetone had only its outer shell dried, while its inner shell remained wet. Although its outer shell was strong, the overall compressive strength was relatively low.

5.2. Scanning electron microscopy and X-ray diffraction

Scanning electron micrographs of the carbon fibre preforms made by using the silica binder after heat treatment at 200 and 800 °C (in argon) and 1100 °C (in argon) showed that the silica binder was rich at the surface and very little was present in the centre at 200 °C. The photographs also show that the silica binder had cracks and exhibited essentially no wetting with the carbon fibres after the heat treatment at 200 °C. After the heat treatment at 800 °C in argon, the surface of the preform showed much better wetting between the carbon fibres and the silica binder, but still some cracks were observed in the binder itself. After the heat treatment at 1100 °C, the surface of the preform was similar to that at 800 °C and good wetting was present between the carbon fibres and the silica binder. However, a non-uniform distribution of the silica binder was observed for the preform after heat treatment at 1100 °C in argon. The non-uniform distribution of the silica binder was due to the cracking of the binder in the preform. The cracking of the binder was attributed to the negative thermal expansion of the tridymite SiO_2 when heated above 800 °C [6]. Hence, the good wetting and uniform distribution of the silica binder for the preform heat treated at 800 °C in argon contributed to a higher compressive strength than those at 200 or 1100 °C (in argon). The silica binder was crystalline at 800 and 1100 °C, but amorphous at 200 °C. That the preform with the silica binder at 800 °C had the highest compressive strength suggested that a crystalline structure was at least not detrimental.

The phosphate A23 binder (with water) resulted in smooth connection among the carbon fibres for the preforms after heat treatment at 200 °C. The binder was in a smaller amount for the carbon fibre preform heat treated at 800 °C in argon, compared to that at 200 °C. Moreover, it formed flakes (size 3–10 μm) adhering to the surface of the carbon fibres. After heat treatment at 1100 °C in argon, the carbon fibre preform showed essentially no binder. This might be because of the non-reactivity of the phosphate binder with the carbon fibres. This non-reactivity enhanced the loss of phosphoric acid (the major part of the phosphate A23 binder). Moreover, the dissociation of type A aluminium metaphosphate into aluminium orthophosphate ($AlPO_4$) and phosphoric oxide (P_2O_5, gas phase) occurred upon heating at 1100 °C in argon. That the amount of the phosphate A23 binder decreased as the heat-treatment temperature increased is consistent with the trend of the compressive strengths of these preforms (Table XIV), i.e. the strongest preform made by using the phosphate A23 binder was the one heat treated at 200 °C.

Scanning electron micrographs of the carbon fibre preforms made by using the acrylic emulsion binder after heat treatment at 200 °C show good fibre wetting and fibre connectivity, which resulted in a high compressive strength after this heat treatment (Table XIV). The low compressive strength of the preform made by using the acrylic emulsion binder after heat treatment at 800 or 1100 °C (in argon) was due to the low melting point of this binder.

The water-glass binder in the preform after heat treatment at 200 °C showed a flake-like morphology, good wetting with the carbon fibres and some cracks. When the preform was heat treated at 800 °C in argon, the water-glass binder had a much smoother morphology (may be due to the softening of the binder upon heating), good wetting and some cracks. After heat treatment at 1100 °C in argon, the water-glass binder in the preform showed a flake-like morphology again and poor wetting with the carbon fibres. This could be due to the decomposition of the water glass (sodium silicate, Na_2SiO_3) to SiO_2 at this temperature (Fig. 11, Part I [1]). The morphology shown by SEM is consistent with the fact that the preform made by using the water-glass binder had its highest compressive strength after heat treatment at 800 °C.

X-ray diffraction patterns of the surface of the preforms made by using the silica, the phosphate A23 (water), the acrylic emulsion and the water-glass binders after heat treatment at 200 °C show the absence of any crystalline phase. This is due to two reasons. One is that the carbon fibres were themselves amorphous; the other is that all these binders were essentially amorphous after heat treatment at 200 °C.

5.3. Atomic absorption analysis

Table XV shows the result of the atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with water (1:15) after drying at 200 °C. The result was shown for four different regions along the radius of the preform. These four regions were equally spaced at a distance of 6.7 mm and were located along a radius from the surface to the centre, as denoted in sequence as A, B, C and D (Fig. 22). Each region had a width of 2 mm along the radius. Both aluminium and phosphorus concentrations increased from the centre toward the surface, as in the case of the SiC whisker preform prepared with the same binder but heated at 500 °C (Table VII). However, the P/Al ratio was higher than in the SiC whisker preform. The value of the P/Al ratio was higher at the centre point (D) than the surface point (A), whereas the reverse trend was observed in the SiC whisker case (Table VII). These observations could be due to the lower heat-treatment temperature of the carbon fibre preform, which resulted in more phosphorus remaining in the preform. It could also be due to the higher filler volume fraction (55%) in the preform, which contained fewer passages for the binder to come out.

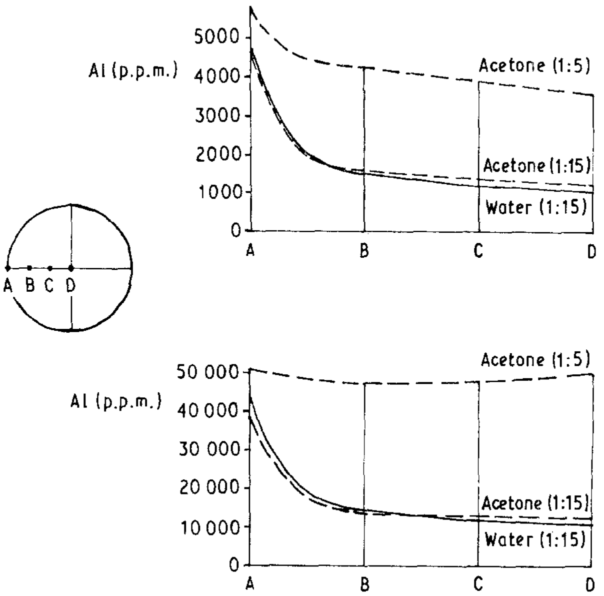

Figure 22 The aluminium and phosphorus concentrations along the radius of the carbon fibre preform made by using the phosphate A23 (1:15 water), A23 (1:15 acetone) and A23 (1:5 acetone) binders.

TABLE XV Result of atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with water (1:15) after drying at 200 °C

Position	Al (p.p.m.) (by weight)	P (p.p.m.) (by weight)	P/Al (by weight)	P/Al (by atom)
A[a]	4690 (530)[b]	43600 (3600)	9.3 (1.3)	8.1 (1.1)
B	1490 (110)	14500 (1000)	9.7 (1.0)	8.5 (0.9)
C	1210 (270)	11900 (900)	9.8 (2.3)	8.6 (2.0)
D[c]	1050 (180)	11100 (1300)	10.6 (2.2)	9.2 (1.9)

[a] Surface
[b] Values in parentheses show the standard deviation.
[c] Centre

Table XVI shows the result of the atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with acetone (1:15) after drying at 200 °C. The aluminium and phosphorus concentrations increased from the centre point (D) toward the surface point (A), as observed for the preform with water (1:15). The P/Al ratio and the uniformity of the phosphorus and aluminium distributions were similar to those of the preform made with water (1:15) (Table XV).

Table XVII shows the result of the atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with acetone (1:5)

TABLE XVI Result of atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with acetone (1:15) after drying at 200 °C

Position	Al (p.p.m.) (by weight)	P (p.p.m.) (by weight)	P/Al (by weight)	P/Al (by atom)
A[a]	4580 (620)[b]	38600 (3100)	8.4 (1.3)	7.3 (1.1)
B	1510 (140)	13700 (1100)	9.1 (1.1)	7.9 (1.0)
C	1350 (170)	13200 (1200)	9.8 (1.5)	8.5 (1.3)
D[c]	1210 (210)	12200 (1500)	10.1 (2.1)	8.8 (1.9)

[a] Surface.

[b] Values in parentheses show the standard deviation.

[c] Centre.

TABLE XVII Result of atomic absorption analysis of the carbon fibre preform made by using the phosphate A23 binder with acetone (1:5) after drying at 200 °C

Position	Al (p.p.m.) (by weight)	P (p.p.m.) (by weight)	P/Al (by weight)	P/Al (by atom)
A[a]	5830 (320)[b]	51400 (4900)	8.8 (1.0)	7.7 (0.8)
B	4180 (230)	47100 (1100)	11.3 (0.7)	9.8 (0.6)
C	3880 (240)	47600 (2100)	12.3 (0.9)	10.7 (0.8)
D[c]	3550 (160)	50000 (1700)	14.1 (0.8)	12.3 (0.7)

[a] Surface.

[b] Values in parentheses show the standard deviation.

[c] Centre.

after drying at 200 °C. A much more uniform binder distribution was observed than the preform made with water (1:15) or acetone (1:15) (Tables XV and XVI). The aluminium content still showed an increasing trend from the centre point, D, to the surface point, A, but, the phosphorus content did not show this trend. The increase of the value of the P/Al ratio from the surface point to the centre point was larger for the preform with acetone (1:5) (Table XVII) than that with water (1:15) (Table XV) or acetone (1:15) (Table XVI). This effect is attributed to the higher binder content in the preform with acetone (1:5) than that of the preform with water (1:15) or acetone (1:15) (Table III). Thus, more binder remained in the centre (D), thereby causing the centre to be still wet after 1 week of drying. The wetness of the binder was associated with a higher phosphorus content and a higher average P/Al ratio.

6. Discussion and conclusion

For discussion of the results, and conclusions, the reader is refered to the corresponding sections in Part III [2] of this series.

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References

1. JENG-MAW CHIOU and D. D. L. CHUNG, *J. Mater. Sci.* **28** (1993) 1135.
2. *Idem, ibid.* **28** (1993) 1471.
3. M. TSUHAKO, *Kagakuno Ryoiki* **37** (1983) 194.
4. M. J. O'HARA, J. J. DUGA and H. D. SHEETS Jr, *Ceram. Bull.* **51** (1972) 590.
5. W. D. KINGERY, *J. Amer. Ceram. Soc.* **33**(8) (1950) 239.
6. W. R. BECK, *ibid.* **32**(4) (1949) 147.

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