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

Part III *Aluminium-matrix composites*

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The use of phosphate binders instead of the widely used silica binder resulted in improved temperature resistance, increased tensile strength and decreased coefficient of thermal expansion. The effects were largest for the phosphate binder which contained the largest amount of phosphoric acid (P/Al atom ratio = 24 in the liquid binder). These effects were probably due to the protection of the SiC whiskers by the binder phases (aluminium metaphosphate or aluminium orthophosphate), the binder–SiC reaction product (SiP_2O_7) and the binder–aluminium reaction product (AlP) from further reaction between the SiC and aluminium. The tensile strength of the composite containing the SiC whisker preform made with the phosphate binder (P/Al atom ratio = 6 or 24 in the liquid binder) was increased after heating at up to 600 °C for 240 h. The silicon phosphate (SiP_2O_7) acted as an *in situ* binder and was primarily responsible for increasing the compressive strength of the preform and increasing the temperature resistance of the composite. The carbon fibre composite containing the preform made by using the phosphate binder (P/Al atom ratio = 24 in the liquid binder) with either water or acetone as the liquid carrier during wet forming of the preform had a higher tensile strength than the carbon fibre composite made by using the silica binder. After composite heat exposure to 600 °C for 14 h, the carbon fibre composite made by using this phosphate binder with acetone as the liquid carrier during wet forming of the preform showed the best temperature resistance, while the carbon fibre composites made by using this phosphate binder with water as the carrier showed the second best temperature resistance, and that made by using silica binder was the worst. The reason for the better effect of the phosphate binder than the silica binder is probably due to the ability of the phosphate binder and the binder–aluminium reaction product (AlP) to protect the carbon fibres from the undesirable reaction between the carbon fibres and aluminium. The lack of a binder–fibre reaction contributed to making the carbon fibre composites less temperature resistant than the SiC whisker composites. The use of a higher binder concentration is attractive for increasing the temperature resistance of the composites. The binder concentration in the preform can be increased by increasing the binder concentration in the slurry used in the wet forming of the preform.

1. Introduction

Aluminium-matrix composites containing either SiC whiskers or short carbon fibres as the reinforcement were fabricated by liquid-metal infiltration of preforms consisting of the reinforcement and a small proportion of a binder. For information on the binders, the reader is referred to Part I [1]. Information on the preforms may be found in Part II [2]. This paper (Part III) relates the binders and preforms to the properties of the resulting composites, for the purpose of obtaining composites of superior mechanical and thermal properties and understanding the origin of the superior properties.

2. Composite fabrication

Aluminium was adopted as the matrix material in this paper mainly due to its processing ease (associated with its low melting temperature), low density, low electrical resistivity, high thermal conductivity, ease of joining, low cost and good machinability. Pure aluminium was further chosen to avoid encountering possible complexities when dealing with the reactions among the reinforcement, the binder (in the preform) and the matrix material. The pure aluminium used was alloy 170.1 (supplied by Roth Bros. Smelting Corp.). Its composition was mainly 99.77% Al, 0.17% Fe and 0.04% Si.

The composite fabrication technique (vacuum infiltration of a liquid metal under an inert gas pressure) used in this study has the advantage of a low temperature (as low as the liquidus) and a low applied pressure during infiltration. The low temperature reduces the interfacial reaction between the liquid metal and the reinforcement during infiltration. The low applied pressure reduces the equipment cost.

The principle of the fabrication technique [3] used in this study is similar to that of the combination of vacuum infiltration and squeeze casting. However, in contrast to squeeze casting, which uses a ram for pressure application, an inert gas is used to press the liquid metal into the preform. The temperature of the molten metal may be as low as the liquidus, in contrast to the much higher melt temperature in squeeze casting. Compared to squeeze casting (100–200 MPa [4]), this fabrication technique (7–18 MPa) needs a lower pressure to force the melt to infiltrate. This is because the preform is under vacuum prior to infiltration; the vacuum eliminates the back pressure in the preform. (This back pressure is usually present in squeeze casting). In addition, the rate of pressure increase is much lower in this technique than in squeeze casting. The main disadvantage of this method compared to squeeze casting is the lower cooling rate, which enhances grain growth in the metal.

The apparatus used in this study for preparing composites is schematically illustrated in Fig. 1 of an earlier paper [3]. The chamber (steel) was evacuated using a mechanical vacuum pump. An inert gas (argon) bottle was connected to the chamber with tubes and a valve. If the pressure of the inert gas in the bottle was lower than 2500 p.s.i. (17.3 MPa), a compressor had to be used to increase the chamber pressure when needed. The chamber wall had to be strong enough to sustain simultaneously high pressures and high temperatures, at least 2500 p.s.i. (17.3 MPa) at 665 °C. The inner wall surface of the chamber was coated with a graphite paste for ease in demoulding. Thermocouples were in contact with the outer wall of the chamber, near to the aluminium alloy in the upper part and the preform at the bottom. Before the high pressure gas was introduced into the chamber the temperature of the aluminium melt was allowed to drop to its liquidus temperature at a low cooling rate (3 °C min^{-1}). The temperature in any part of the chamber was approximately the same. The heating element was made of graphite.

The process used for composite fabrication is schematically illustrated in Fig. 2 of an earlier paper [3]. The process may be divided into seven steps, which are described below.

1. The aluminium ingot and the preform were put in the chamber. The chamber was then sealed and evacuated to a pressure of 50–200 mtorr (9.7×10^{-4}–38.7×10^{-4} p.s.i., or 6.7–26.7 Pa).

2. The chamber and its charges were superheated 50–100 °C above the liquidus temperature of the alloy. In the mean time, evacuation continued.

3. The temperature was maintained for a period of time to ensure that the alloy melted completely and that the temperature of any part of the chamber was approximately equal.

4. The power input was gradually lowered until the temperature dropped to the liquidus or near to the liquidus at the cooling rate of 0.5–3.0 °C min^{-1}. Evacuation continued at the same time.

5. While the temperature was maintained, the evacuation was stopped. The valve connected to the inert gas bottle was opened. A pressure of 1000–2500 p.s.i. (6.9–17.3 MPa) was applied to the surface of the melt to force the melt to penetrate the porous preform completely. This temperature is called the infiltration temperature, T_p. The pressure applied to force the melt to infiltrate the preform is called the infiltration pressure. A time of 40–80 s was needed to reach the pressure of 2000 p.s.i. (13.8 MPa) used in this work.

6. Once the predetermined pressure was reached, the electricity supply to the heating element was cut off. In order to increase the cooling rate of the chamber, a cooling water jacket outside the chamber was used. The pressure was maintained during the solidification period and the cooling period afterwards.

7. When the temperature was 30–50 °C below the solidus, the outlet valve was opened to release the inert gas. Premature release would result in shrinkages, cavities and cracks in the composite. The temperature continued to drop until it was below 300 °C. The lid of the chamber was then opened. The composite material was then demoulded from the chamber.

The infiltration temperature, T_p, used was 665 °C. The infiltration pressure used was 2000 p.s.i. (13.8 MPa). The gas used was argon, due to its inertness and availability. Nitrogen was not used because it may react with the aluminium melt to form aluminium nitride (AlN).

3. Al/SiC$_W$ composite characterization

3.1. Structure

Fig. 1 shows scanning electron micrographs of polished and etched sections of preforms made by using the silica and phosphate A23 binders and heat treated at 500 °C. The whisker distribution was quite uniform for both composites. Some uninfiltrated spots (size 0.1 μm) were found in both composites in regions where the whiskers clustered. The porosity was less than 0.1%.

3.2. Mechanical properties

Tensile testing was performed using a hydraulic mechanical testing system (MTS). Dogbone-shaped samples were obtained by cutting the as-cast composite cylinder parallel to the cylindrical axis to form two plates, which were then machined by double-side grooving, as illustrated in Fig. 2. The dimensions of the samples are shown in Fig. 3. The Young's modulus was measured using a strain gauge at low loads. The 0.2% offset yield strength was taken as the yield strength. The ductility was determined by drawing two parallel lines marking the gauge length on the

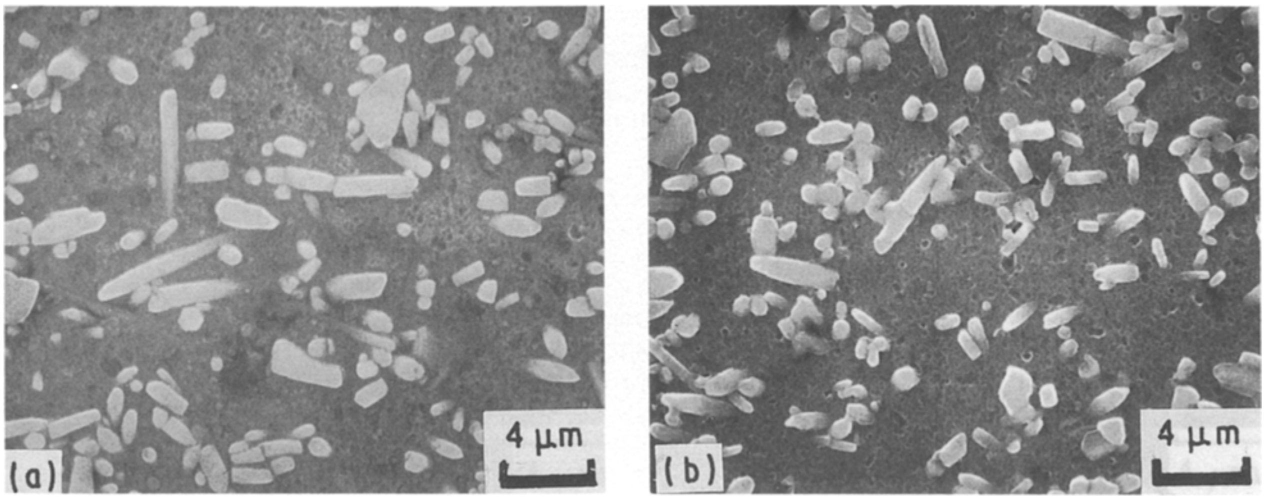

Figure 1 Scanning electron microscope photographs of the typical polished SiC whisker composites (containing preforms made by using (a) the silica binder and (b) the phosphate A23 binder after heat treatment at 500 °C) after etching.

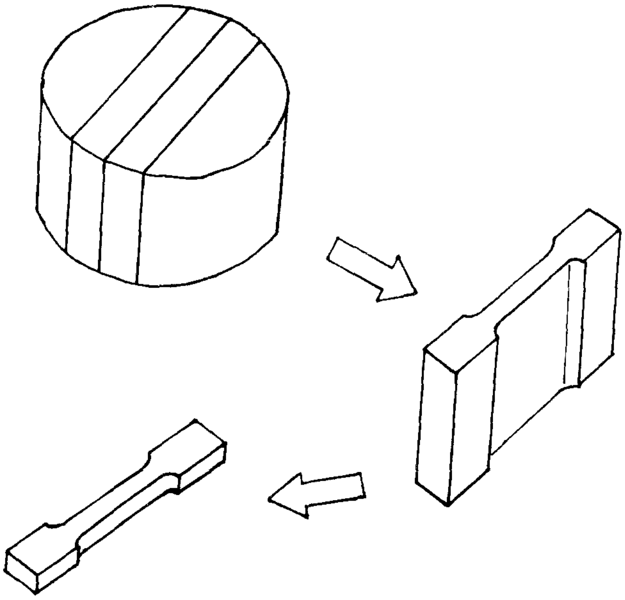

Figure 2 Procedure for preparing the tensile test samples.

sample and measuring the distance between the lines before and after tensile testing using calipers.

High-temperature tensile testing was performed using the same method, except that a resistance furnace was placed around the sample. The temperature accuracy was ± 10 °C. Each sample was preheated in air at the test temperature for 100 h prior to testing, in order to allow time for the interfacial reaction between the reinforcement and the matrix to take place [5].

Table I shows the variation with the preform heat-treatment temperature of the tensile strength, yield strength, Young's modulus and ductility of the composites containing the preform which was made with either the silica or phosphate A23 binder. For either silica or phosphate A23 binder, the tensile strength was highest for the MMC containing the preform after heat treatment at 500 °C, lowest at 1100 °C in air and second lowest at 1100 °C in argon. For each heat-treatment condition, the tensile strength was higher for the MMC with the phosphate A23 binder than the MMC with the silica binder. The yield strength did not vary much with the binder species or the preform heat-treatment condition, except that an outstandingly high yield strength was obtained for the MMC containing the preform made with the phosphate A23 binder and heat treated at 1100 °C in air. This is due to the formation of SiO_2 on the SiC whiskers during preform heat treatment (Fig. 15, Part II [2]). The presence of the SiO_2 (with a low coefficient of thermal expansion) induced more dislocations near the whiskers (upon cooling during the composite fabrication) due to the thermal expansion mismatch. The modulus also did not vary much with the binder species or the preform heat-treatment condition, except that the modulus was lower when the preform heat-treatment temperature was beyond 800 °C (for the silica binder) or 500 °C (for the phosphate A23 binder). This effect on the modulus was probably due to the binder–whisker reaction (such as the formation of SiP_2O_7 or SiO_2 for the case of the phosphate binder), which deteriorated the SiC whiskers slightly. For almost all preform heat-treatment conditions, the ductility was higher for the MMC with the phosphate binder than the MMC with the silica binder. For each binder, the ductility decreased with increasing preform heat-treatment temperature beyond 500 °C and was higher for heat treatment in argon than in air. The formation

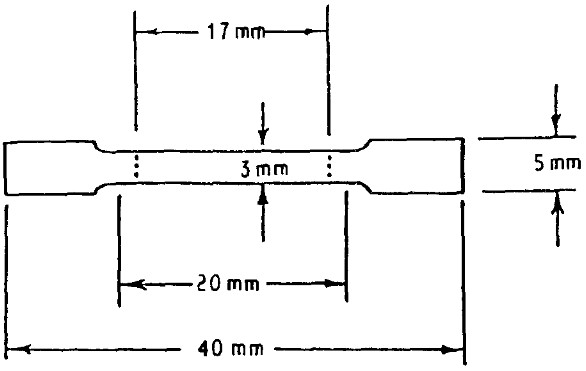

Figure 3 Specimen geometry for tensile testing.

TABLE I Mechanical properties of SiC whisker-reinforced metal-matrix composites and their variation with the preform heat-treatment temperatures

Binder	Preform heat treatment (°C)	SiC_w vol. fraction (%)	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Ductility (%)
Silica	200	22.2	306.0 (9.5)[a]	139.5 (5.7)	105.2 (8.8)	2.1 (0.7)
Silica	500	22.5	331.9 (9.3)	168.2 (6.3)	110.1 (5.2)	2.6 (0.4)
Silica	800	21.8	311.8 (33.0)	171.6 (7.1)	105.3 (2.3)	2.1 (0.7)
Silica	1100 (air)	22.6	252.8 (49.5)	161.2 (5.4)	93.9 (17.8)	0.7 (0.2)
Silica	1100 (argon)	21.8	288.4 (12.2)	148.2 (6.5)	87.6 (3.8)	2.5 (0.5)
Phosphate A23	200	22.4	323.7 (13.3)	142.8 (9.3)	116.0 (7.8)	2.7 (1.1)
Phosphate A23	500	22.5	368.4 (14.4)	155.3 (7.4)	116.7 (4.5)	2.9 (0.3)
Phosphate A23	800	22.5	343.0 (6.3)	157.8 (9.9)	97.5 (7.2)	2.3 (0.5)
Phosphate A23	1100 (air)	22.8	313.1 (23.3)	231.9 (12.7)	96.4 (2.7)	1.4 (0.4)
Phosphate A23	1100 (argon)	22.3	318.9 (20.9)	163.4 (6.8)	96.2 (8.4)	2.4 (0.7)

[a] Values in parentheses show the standard deviation.

TABLE II Mechanical properties of SiC whisker-reinforced metal-matrix composites with the variation of the preform binder species

Binder	Preform heat treatment (°C)	Composite heat treatment	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Ductility (%)
Silica	500	Without heating	331.9 (9.3)[a]	168.2 (6.3)	110.1 (5.2)	2.6 (0.4)
Phosphate A03	500	Without heating	336.5 (13.2)	135.6 (5.8)	106.9 (5.5)	3.6 (0.7)
Phosphate A03	1200 (argon)	Without heating	335.9 (5.6)	142.4 (1.1)	95.2 (4.2)	3.9 (0.5)
Phosphate A06	500	Without heating	345.6 (8.7)	152.7 (5.6)	119.4 (6.8)	3.1 (0.7)
Phosphate A23 (water)	500	Without heating	368.4 (14.4)	155.3 (7.4)	116.7 (4.5)	2.9 (0.3)
Phosphate A23 (acetone)	500	Without heating	358.0 (11.0)	149.3 (8.0)	114.4 (6.3)	2.9 (0.7)
Phosphate MAP	500	Without heating	324.3 (12.1)	133.1 (12.3)	98.7 (10.8)	2.8 (0.5)

[a] Values in parentheses show the standard deviation.

of SiO_2 in the preforms heat treated at 1100 °C in air is probably the main cause for the decrease in the ductility.

Table II shows the variation with the preform binder species of the tensile strength, yield strength, Young's modulus and ductility of the composites. The binders were silica, phosphate A03, phosphate A06, phosphate A23 and phosphate MAP ($P/Al = 3$). For the composites with the preforms heat treated at 500 °C, the tensile strength and yield strength of the composites made by using the phosphate binders increased as the P/Al atom ratio of the binder increased from 3 to 6, and to 23. On the other hand, the ductility of the composites decreased as this ratio increased. The composite containing the preform made by using the silica binder showed similar tensile strength and modulus compared to those of the composite using the phosphate A03 (500 °C) binder, but the yield strength was higher and the ductility was lower than all the phosphate binder counterparts. This may be because the silica binder (with a low coefficient of thermal expansion) induced more dislocations near the whiskers in the cooling step of the composite fabrication. Of all the 500 °C phosphate binders, MAP (which had the same value of P/Al atom ratio as A03) gave composites of the lowest tensile strength, yield strength, modulus and ductility. This may be due to the presence of the visible impurity in the as-received phosphate MAP solution.

The composite containing the preform made by using the phosphate A03 binder after heat treatment at 1200 °C in argon showed comparable tensile strength, yield strength and ductility as its counterpart with the preform heat treated at 500 °C. However, this composite showed a lower Young's modulus. This is also probably due to the binder–whisker reaction, which was more severe at the higher temperature.

The composite containing the preform made by using the phosphate A23 binder with acetone (1:15) showed a lower tensile strength than its counterpart with water (1:15), but still a higher tensile strength than the composite containing the preform made by using the phosphate A06 binder. The lower tensile strength of the composite with acetone (1:15) compared to that with water (1:15) was due to the smaller amount of phosphorus stored in the binder (Table VII, Part II [2]). The use of acetone instead of water did not have any clear effect on the yield strength, Young's modulus or ductility.

In order to investigate the temperature resistance of the composites, the composites were heated in air at either 400 or 600 °C for 10 days and the tensile properties were tested before and after the heating. Table III shows the results obtained for composites made by using silica, phosphate A03, phosphate A06, phosphate A23 and phosphate MAP binders. The heating decreased the tensile strength of the composites made by using the silica binder, had negligible effects on the tensile strength of the composites made by using the phosphate A03 and MAP binders, but increased those of composites made by using the phosphate A06 and phosphate A23 binders. The effect was particularly significant for the heating at 600 °C and for the composites made by using the phosphate A23 binder. Table III also shows that the tensile strength without heating was higher for composites made by using the phosphate A23 binder than those made by using the silica or other phosphate binders. The tensile strength was not much changed for the composites made by using the phosphate A03 or phosphate MAP binders after heating at 600 °C.

The yield strength of the composite containing the preform made by using the silica binder (with preform heat treatment at 500 °C) was decreased after composite heat exposure at 400 or 600 °C for 240 h. This is attributed to the strain relief after the long-term high-

TABLE III Mechanical properties of SiC whisker-reinforced metal-matrix composites after heat treatments

Binder	Preform heat treatment (°C)	Composite heat treatment (°C, h)	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Ductility (%)
Silica	500	Without heating	331.9 (9.3)[a]	168.2 (6.3)	110.1 (5.2)	2.6 (0.4)
Silica	500	400, 240	309.7 (20.9)	149.4 (6.7)	107.8 (9.5)	2.4 (0.6)
Silica	500	600, 240	291.8 (22.4)	143.5 (6.7)	106.5 (4.4)	2.8 (0.3)
Phosphate A03	500	Without heating	336.5 (13.2)	135.6 (5.8)	106.9 (5.5)	3.6 (0.7)
Phosphate A03	500	600, 240	340.3 (5.4)	141.5 (11.0)	108.2 (7.0)	3.0 (0.5)
Phosphate A03	1200 (argon)	Without heating	335.9 (5.6)	142.4 (1.1)	95.2 (4.2)	3.9 (0.5)
Phosphate A03	1200 (argon)	600, 240	339.6 (6.1)	153.3 (1.3)	94.2 (4.3)	3.3 (0.9)
Phosphate A06	500	Without heating	345.6 (8.7)	152.7 (5.6)	119.4 (6.8)	3.1 (0.7)
Phosphate A06	500	600, 240	362.5 (9.5)	146.8 (5.6)	107.3 (5.5)	3.2 (0.8)
Phosphate A23 (water)	500	Without heating	368.4 (14.4)	155.3 (7.4)	116.7 (4.5)	2.9 (0.3)
Phosphate A23 (water)	500	400, 240	360.3 (10.3)	143.3 (7.0)	109.2 (8.9)	2.5 (0.8)
Phosphate A23 (water)	500	600, 240	391.4 (6.4)	153.3 (5.6)	110.7 (4.6)	2.6 (0.4)
Phosphate A23 (acetone)	500	Without heating	358.0 (11.0)	149.3 (8.0)	114.4 (6.3)	2.9 (0.7)
Phosphate A23 (acetone)	500	600, 240	373.5 (24.5)	156.8 (5.5)	109.2 (4.7)	2.4 (0.4)
Phosphate MAP	500	Without heating	324.3 (12.1)	133.1 (7.5)	98.7 (9.7)	2.8 (0.7)
Phosphate MAP	500	600, 240	322.6 (11.2)	146.4 (12.3)	98.0 (10.8)	2.3 (0.5)

[a] Values in parentheses show the standard deviation.

temperature exposure (or annealing). That the effect of the heating was not significant for the case of the phosphate binders was probably due to the binder–aluminium reaction, which modified the thermal expansion mismatch situation.

The Young's modulus of the composite containing the preform made by using the phosphate A03 binder (with preform heat treatment at 1200 °C in argon) was low before and after the composite heat exposure at 600 °C for 240 h. This is because the binder–whisker reaction during the preform heat treatment deteriorated the SiC whiskers. The low modulus for the composite containing the preform made by using the phosphate MAP binder was probably due to the presence of the visible impurity in the as-received phosphate MAP solution. The moduli of the other composites showed similar values and no trend. This is due to the fact that the modulus was measured at low loads. At a low load, the whisker bonding for each composite had enough strength to transfer the load. The effects of the binder species or heating on the ductility were not significant enough to show any trend.

The composite containing the preform made by using the phosphate A23 binder with acetone (1:15) showed a slightly lower tensile strength than its counterpart with water (1:15), in spite of the more uniform binder distribution (aluminium and phosphorus concentrations in Table VII, Part II [2]) in the former. This was due to the smaller amount of the stored phosphoric acid (or phosphorus in a certain form) for the composite containing the preform with acetone than its counterpart with water. The smaller amount of the extra phosphoric acid (or phosphorus in a certain form) was indicated by the smaller weight loss (Table II, Part II [2]) and smaller P/Al ratio (Table VII, Part II [2]) of the binder with acetone compared to that of the binder with water. Water and acetone gave little difference to the yield strength, Young's modulus and ductility of the composites.

In general, these results show that the temperature resistance of the composites made by using all the different kinds of phosphate binders was better than that of the composites made by using the silica binder. In particular, the composite made by using the phosphate A06 and A23 binders not only maintained but increased its ultimate tensile strength after heating. Fig. 4 shows the typical stress–strain curves of these composites. These curves show a similar shape with essentially the only difference in the ultimate tensile strength. This is because they had the same type and the same volume fraction of the reinforcement and the same aluminium matrix. Differences in the binder and in the composite heat treatment caused the variation of the tensile strength of these composites.

SEM was used to examine the fracture surfaces of the composites containing the preform which was made with the silica binder and heat treated at 500 °C. More whisker pull-out was observed for the composite after heat treatment at 600 °C (for 10 days) than that before heating. Because more whisker pull-out means a lower interfacial bonding strength, the long-term heating of the composite at 600 °C might have deteriorated the interface. This is consistent with the fact that heating at 600 °C decreased the tensile strength of the composite containing the preform made with the silica binder.

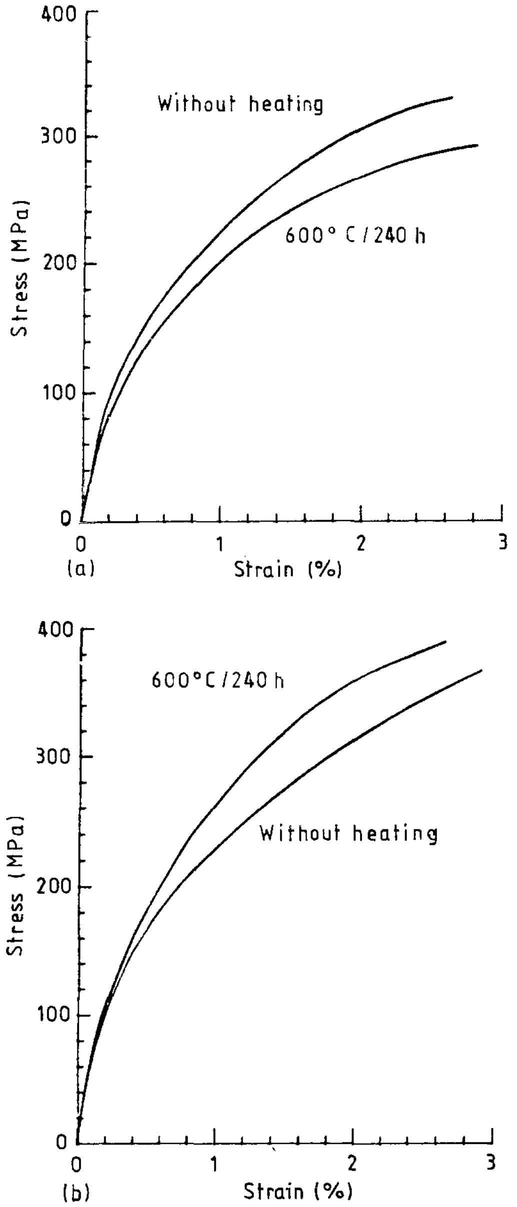

Figure 4 The stress–strain curves for SiC whisker composites containing the preforms made by using (a) the silica binder, and (b) the phosphate A23 binder after heat treatment at 500 °C. For each case, curves are shown for the composite without heat treatment and that after heat treatment at 600 °C for 240 h.

The fracture surface of the composite containing the preform which was made with the silica binder and heat treated at 1100 °C in air has less dimples than that of the composites containing the preform heat treated at 500 °C. This is consistent with the lower ductility of this composite observed in tensile testing. A possible cause for this is related to the formation of the brittle cristobalite SiO_2 in the heat treatment at 1100 °C in air.

The fracture surfaces of the composites containing the preform which was made with the phosphate A23 binder and heat treated at 500 °C were also examined. In contrast to that of the composite with the silica binder, less whisker pull-out was observed for the composite after heat treatment at 600 °C (for 10 days) than that before heating. This means that the long-term heating at 600 °C increased the interfacial bonding strength, which in turn resulted in a higher ultimate tensile strength.

The fracture surfaces of the composites containing the preforms made with the phosphate A23 binder and heat treated at 1100 °C in air and in argon were compared. The composite containing the preform heat treated in air had a more brittle appearance than the preform heat treated in argon. Again, the presence of cristobalite SiO_2 in the composite containing the preform heat treated at 1100 °C in air is the main cause for this. In contrast, the composite containing the preform heat treated in argon showed the usual dimple-type fracture surface. This is consistent with the ductility from the tensile testing result.

The fracture surfaces of the composites containing the preforms which were made with the phosphate binders A03, A06 and MAP (heat treated at 500 °C) after composite heat treatment at 600 °C for 10 days show the typical dimple morphology with some whisker pull-out. The amount of whisker pull-out was related to the tensile strength of the composite. Of these three composites, the composite made with the phosphate A06 binder has the least pull-out (with the highest tensile strength) and the composite made with the phosphate MAP binder had the most pull-out (with the lowest tensile strength). Comparison of the composites (heat exposed at 600 °C for 240 h) made with the phosphate A03, A06 and MAP binders and the composite (heat exposed at 600 °C for 240 h) made with the phosphate A23 binder shows that the composite made with the phosphate A23 binder had almost no whisker pull-out (less than the composites with the phosphate A03, A06 and MAP binders) and consistently had the highest tensile strength of all the composites.

The fracture surfaces of the composites containing the preform which was made with the phosphate A03 binder and heat treated at 1200 °C in argon showed a morphology similar to that of its counterpart with the preform heat treated at 500 °C. This is also consistent with the similar tensile strength of these composites (Table III).

3.3. Reaction between binders, SiC whiskers and aluminium

The reason for the composites containing the preform made by using the phosphate binders having higher tensile strength and better temperature resistance than the composite made by using the silica binder, was probably associated with the reaction between the phosphate binder and the matrix aluminium. The possible reaction between the phosphate binders and the aluminium was explored by making a sandwich containing the wet undiluted binder in between two sheets of aluminium foil (cleaned by acetone). The sandwich was then heat treated at temperatures and pressures identical to those used for making the MMCs. The sandwich after processing contained around 30–70 vol % Al (i.e. the aluminium was in excess of that needed for the binder–aluminium reaction). Fig. 5 shows the X-ray diffraction (XRD) patterns of the processed sandwiches. All the sandwiches made by using the phosphate binders showed the formation of a reaction product, namely aluminium phosphide (AlP), in addition to the binder and aluminium phases. On the other hand, the sandwich made by using the silica binder showed no reaction product at all. Table IV shows the amount of the aluminium phosphide (AlP) relative to that of the binder (type A and type B $Al(PO_3)_3$ together). This ratio was calculated by dividing the sum of the intensities of all the peaks from the aluminium phosphide (AlP) by the sum of the intensities of all the peaks form the binder phases (type A and type B $Al(PO_3)_3$). It was highest for the phosphate A99 binder, second highest for the phosphate A23 binder, and lowest for the phosphate A03 binder. The highest value for the phosphate A99 binder shows that the phosphoric acid rather than $Al(PO_3)_3$ was responsible for the reaction with aluminium to form AlP.

TABLE IV The relative amount of the reaction product to that of the binder in the aluminium–binder–aluminium sandwich

Binder	AlP/(A + B)
Phosphate A03	0.086 ± 0.001
Phosphate A06	0.184 ± 0.002
Phosphate A12	0.131 ± 0.002
Phosphate A23	0.261 ± 0.003
Phosphate A99	0.286 ± 0.003
Phosphate MAP	0.180 ± 0.002

A, aluminium metaphosphate $Al(PO_3)_3$ (A); B, aluminium metaphosphate $Al(PO_3)_3$ (B); AlP, aluminium phosphide (AlP).

3.4. Thermal expansion of composites

The coefficient of thermal expansion (CTE) of the composites was measured after annealing at 600 °C for either 2 or 240 h, using the DuPont Instruments TMA2940 thermomechanical analyser operated from 35–600 °C at a heating rate of 5 °C min^{-1}. Table V shows the mean CTE for various temperature ranges. The CTE was lower for composites made by using the phosphate A23 binder than composites made by using the silica binder for the same annealing time at 600 °C and for the same test temperature range. The difference in CTE between the two binder cases increased with increasing test temperature. The CTE was not much changed by increasing the annealing time at 600 °C from 2 h to 240 h.

4. Al/C_f composite characterization

4.1. Effect of binders on the mechanical properties

Four types of carbon fibre composites were fabricated and tested. The first is the composite containing the carbon fibre preform made by using the silica binder,

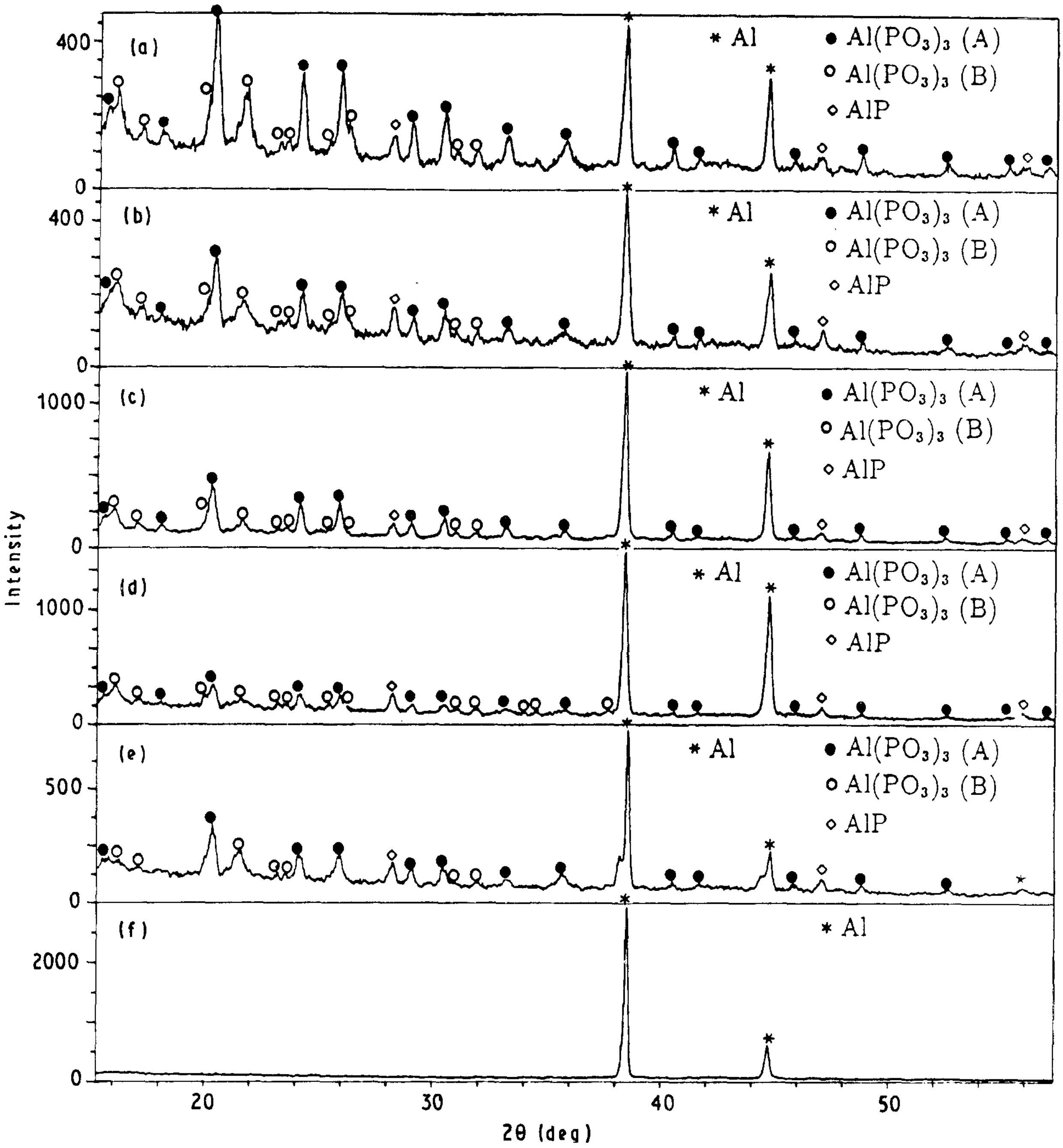

Figure 5 XRD patterns of the MMC-fabrication-processed aluminium–binder–aluminium sandwich. (a) Phosphate A03, (b) phosphate A06, (c) phosphate A12, (d) phosphate A23, (e) phosphate MAP and (f) silica.

TABLE V Coefficient of thermal expansion of the SiC whisker-reinforced metal-matrix composites

	Annealing (°C, h)	Mean CTE (10^{-6} °C^{-1})					
		35–100 °C	35–200 °C	35–300 °C	35–400 °C	35–500 °C	35–600 °C
Silica binder	600, 2	19.5	20.7	23.8	26.8	27.4	28.5
	600, 240	19.7	20.4	22.9	26.3	28.6	31.4
Phosphate binder A23	600, 2	19.0	19.6	21.8	24.4	25.7	26.5
	600, 240	18.6	19.3	21.5	24.9	26.7	29.7

the second one is that containing the preform made by using the phosphate A23 binder with water (binder/water ratio of 1/15) as the carrier in the slurry, and the third and fourth ones are those containing preforms made by using the phosphate A23 binder with acetone (binder/acetone ratio of 1/15 and 1/5, respectively) as the carrier in the slurry. All the composites contained 55 vol % short carbon fibres. Table VI shows the mechanical properties of these composites. The tensile strength was higher for the composites containing the

TABLE VI Mechanical properties of carbon fibre composites with the variation of preform binder species

Binder	Preform heat treatment (°C)	Composite heat treatment	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Ductility (%)
Silica	200	Without heating	91.6 (9.7)[a]	67.8 (0.5)	54.3 (4.0)	1.3 (0.3)
Phosphate A23 (1:15 water)	200	Without heating	105.4 (5.2)	66.2 (5.4)	52.9 (2.8)	1.8 (0.4)
Phosphate A23 (1:15 acetone)	200	Without heating	101.3 (5.7)	68.4 (3.2)	52.1 (2.4)	1.1 (0.3)
Phosphate A23 (1:5 acetone)	200	Without heating	108.6 (10.3)	80.8 (2.3)	53.6 (1.7)	1.6 (0.4)

[a] Values in parentheses show the standard deviation.

preform made by using the phosphate A23 binder with either water or acetone than that made by using the silica binder. The composite containing the carbon fibre preform made by using the phosphate A23 binder with acetone (1:15) showed tensile strength, yield strength, Young's modulus and ductility that were similar to its counterpart with water (1:15). The use of acetone or water gave similar effects. The composite containing the carbon fibre preform made by using the phosphate A23 binder with acetone (1:5) had a higher yield strength than the other three composites. This is due to the larger binder amount and the more significant binder–aluminium reaction resulting from the higher phosphorus concentration in this composite (Table XVII, Part II compared to Tables XVI and XV, Part II [2]). The Young's moduli of these four composites were similar and were all lower than that of aluminium (62 GPa). This is because the small degree of strengthening resulted from the small aspect ratio of the carbon fibres, together with the low carbon fibre bonding strength, was not enough to make up for the loss of the original contribution of 55 vol % aluminium to the modulus. The ductilities of these composites had little differences. The tensile strength of these four composites were all higher than that of aluminium (65 MPa). This is because the high density of the dislocations (due to the thermal expansion mismatch between aluminium and carbon fibres) in the composites was enough to compensate for the loss of the original contribution of 55 vol % Al to the strength.

4.2. Effect of long-term high-temperature exposure on the mechanical properties

All the carbon fibre composites were exposed to 600 °C for 2, 14 and 240 h in order to investigate the effect of the binder species on the temperature resistance of the composites. Table VII shows the mechanical properties of the carbon fibre composites after heat treatment at 600 °C for 2, 14 and 240 h. The results show that the composite containing the preform made by using the silica binder decreased to about 91% of its original tensile strength after 2 h heat treatment and the other three composites, which contained the preform made by using the phosphate A23 binder, had not much change after this heat treatment. When these composites were heat treated at 600 °C for 14 h, the composite containing the preform made by using the silica binder showed a large decrease in the tensile strength (down to about 60% of its original strength) and the composite containing the preform made by using the phosphate A23 binder with water also showed a large decrease in the tensile strength (down to about 62% of its original strength). On the other hand, the composite containing the preform made by using the phosphate A23 binder with acetone (1:15) and (1:5) maintained 73% and 85%, respectively, of its original tensile strength. After heat treatment at 600 °C for 240 h, all the composites had only 50%–60% of their original tensile strength before heating. The yield strength showed a similar trend but not as clearly as that shown by the tensile strength, probably due to the narrower range of variation. The Young's moduli of these composites generally decreased when the heat-treatment period increased. No trend was observed for the ductility of these composites as a function of heat treatment time at 600 °C.

That the phosphate A23 (1:15 acetone) binder gave carbon fiber composites of better temperature resistance than the phosphate A23 (1:15 water) binder is probably due to the more uniform binder concentration (aluminium and phosphorus concentrations, see Tables XVI and XV, Part II [2]) in composites of the former, though the former had a lower P/Al ratio. That the phosphate A23 (1:5 acetone) binder gave composites of better temperature resistance than the phosphate A23 (1:15 acetone) binder is due to the higher binder content and probably also the higher P/Al ratio in composites of the former. The higher P/Al ratio enhanced the binder–aluminium reaction.

4.3. Metallography and fractography

Optical microscopy was used to examine the polished surface of the composite containing the carbon fibre preform made by using the phosphate A23 binder with acetone. The composite without heat treatment showed good wetting between the carbon fibres and aluminium and no interfacial reaction. However, the composite after heat treatment at 600 °C for 240 h showed a totally different microstructure, as most of the carbon fibres had disappeared, leaving some regions without fibres. Some of these regions were filled

TABLE VII Mechanical properties of carbon fibre composites before and after heat treatments

Binder	Preform heat treatment (°C)	Composite heat treatment (°C, h)	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Ductility (%)
Silica	200	Without heating	91.6 (9.7)[a]	67.8 (0.5)	54.3 (4.0)	1.3 (0.3)
Silica	200	600, 2	83.5 (0.9)	65.6 (2.3)	52.7 (3.7)	1.2 (0.2)
Silica	200	600, 14	54.8 (1.3)	54.4 (1.7)	49.6 (6.2)	1.5 (0.5)
Silica	200	600, 240	57.7 (11.7)	48.2 (2.2)	47.4 (4.8)	1.3 (0.8)
Phosphate A23 (1:15 water)	200	Without heating	105.4 (5.2)	66.2 (5.4)	52.9 (2.8)	1.8 (0.4)
Phosphate A23 (1:15 water)	200	600, 2	101.2 (4.9)	65.4 (2.7)	48.3 (3.4)	1.1 (0.3)
Phosphate A23 (1:15 water)	200	600, 14	65.2 (6.8)	59.5 (2.5)	49.4 (1.4)	1.3 (0.6)
Phosphate A23 (1:15 water)	200	600, 240	52.0 (7.2)	47.8 (3.7)	45.1 (7.2)	1.4 (0.2)
Phosphate A23 (1:15 acetone)	200	Without heating	101.3 (5.7)	68.4 (3.2)	52.1 (2.4)	1.1 (0.3)
Phosphate A23 (1:15 acetone)	200	600, 2	105.7 (6.8)	62.8 (2.2)	51.7 (1.7)	1.4 (0.4)
Phosphate A23 (1:15 acetone)	200	600, 14	74.4 (8.2)	60.2 (3.0)	49.0 (3.9)	1.5 (0.5)
Phosphate A23 (1:5 acetone)	200	Without heating	108.6 (10.3)	80.8 (2.3)	53.6 (1.7)	1.6 (0.4)
Phosphate A23 (1:5 acetone)	200	600, 2	109.1 (8.8)	78.9 (1.7)	52.8 (1.9)	1.3 (0.4)
Phosphate A23 (1:5 acetone)	200	600, 14	92.2 (7.2)	65.6 (3.6)	49.4 (2.5)	1.6 (0.8)
Phosphate A23 (1:5 acetone)	200	600, 240	57.0 (13.5)	51.9 (4.2)	47.5 (4.3)	1.4 (0.5)

[a] Values in parentheses show the standard deviation.

with aluminium. Similar observations were made on composites containing the carbon fibre preforms made by using the silica binder and phosphate A23 binder with water.

The polished surface of the composites containing the carbon fibre preform made by using the silica binder or the phosphate A23 binder with acetone were similarly examined after heat treatment at 600 °C for 2 h. The composite containing the preform made by using the silica binder showed some degradation of the surface of the carbon fibres, but the composite made by using the phosphate A23 binder showed clean interfaces surrounding the carbon fibres. Consistent with this observation was the 9% decrease of the tensile strength of the composite containing the preform made by using the silica binder after the heat treatment at 600 °C for 2 h and the absence of any effect for the case with the phosphate A23 binder. An interfacial reaction occurred between the carbon and the aluminium. The reaction between carbon and aluminium was reported to form aluminium carbide (Al_4C_3) [6]. The polished surface of the composite made by using the phosphate A23 binder with water was similar to that of the composite made by using the phosphate A23 binder with acetone.

The fracture surface of the composite made by using the silica binder showed fibre pull-out for the composite without the heat treatment, but cleavage within the carbon fibres was observed along the longitudinal direction of the carbon fibre. The low aspect ratio (about 10) of the carbon fibres and the fibre cleavage caused the strengthening effect of the carbon fibres on the composite to be small, even when a high volume fraction of carbon fibres was used. When the composite was heat treated at 600 °C for 14 h, the fracture surface showed much fibre pull-out. The fibre pull-out was accompanied by the presence of a rough morphology at the fibre–matrix interface, which was not found for the composite without heat treatment. This indicates that an interfacial reaction occurred during the high-temperature heat treatment, which, in turn, degraded the bonding strength of the carbon fibres and decreased the tensile strength of the composite. This is consistent with the fact that the tensile strength of the composite decreased to 60% of its original value after heat treatment at 600 °C for 14 h. The fracture surface of the composite after heat treatment at 600 °C for 240 h showed that all the pull-out interfaces were very rough and no carbon fibre remained in the holes after fibre pull-out. This is consistent with the optical microscope observation of the polished surface for the same sample. The tensile strengths of the composites heated at 600 °C for 14 and 240 h were similar, although different fracture morphologies were observed.

For the composite made by using the phosphate A23 binder with water, the fracture surface of the composite without heat treatment showed no fibre pull-out. Some fibre pull-out was found on the fracture surface of the composite after heat treatment at 600 °C for 14 h. The amount of fibre pull-out was less than that of the composite made by using the silica binder after heat treatment at the same condition. The roughness of the pull-out interface was also less for the composite made by using the phosphate A23 binder with water than that of the composite made by using the silica binder. This is consistent with the result of tensile testing, which shows that the composite made by using the phosphate A23 binder with water had a higher tensile strength than the composite made by using the silica binder. The fracture surface of the composite after heat treatment at 600 °C for 240 h showed a morphology similar to that of the composite made by using the silica binder after heat treatment at the same condition.

For the composite made by using the phosphate A23 binder with acetone, no fibre pull-out was found for the composite without heat treatment and after heat treatment for 14 h. This is different from those of the last two composites (those made by using the silica and phosphate A23 with water), which showed some fibre pull-out after the same heat-treatment condition. This is consistent with the fact that the composite made by using the phosphate A23 binder with acetone maintained its tensile strength after heat treatment at 600 °C for 14 h. Again, the fracture surface of the composite after heat treatment at 600 °C for 240 h showed a morphology similar to that of the composites made by using the silica and phosphate A23 (with water) binders after the same heat treatment. This is consistent with the result that all of the composites after heat treatment at 600 °C for 240 h showed similar values of the tensile strength.

5. Discussion

5.1. Role of the binders in SiC whisker composites

If the tensile strength value of the composite containing the preform made by using the silica binder after preform heat treatment at 500 °C is taken as the reference (or bases) value, then the use of the phosphate A06 or A23 binder increased the tensile strength of the composites whereas the use of the phosphate A03 binder (after preform heat treatment at 500 °C in air or 1200 °C in argon) did not increase the tensile strength of the composite (Table II).

When the composite was heated at 600 °C for 240 h, (i) the use of the silica binder decreased the tensile strength of the composite, (ii) the use of the phosphate A03 binder (after preform heat treatment at 500 °C in air or 1200 °C in argon) maintained the tensile strength of the composite and (iii) the use of the phosphate A06 or A23 binder further increased (in addition to the already increased amount before the heat treatment at 600 °C for 240 h) the tensile strength of the composite (Table III).

Therefore, the use of the phosphate A03 binder (after preform heat treatment at 500 °C in air or 1200 °C in argon) gave a contribution which is the maintenance of the tensile strength of the composite. However, the use of the phosphate A06 or A23 binders gave two contributions, which are (i) the increase in the tensile strength of the composite before heat exposure at 600 °C for 240 h and (ii) the further increase of (not just maintaining) the tensile strength of the composite after heat exposure at 600 °C for 240 h.

Table VIII shows the presence or absence of silica or phosphate binders and the associated reaction product phases in the SiC whisker composites. The silica binder showed no reaction product. For the case of the phosphate A03 binder after preform heat treatment at 500 °C, the aluminium metaphosphate ($Al(PO_3)_3$) was the major phase accompanied by the presence of aluminium phosphide (AlP). For the case of the phosphate A03 binder after heat treatment at 1200 °C in argon, the aluminium orthophosphate ($AlPO_4$) was the only phase present; the aluminium orthophosphate ($AlPO_4$) was stable enough and would not react with the aluminium to form aluminium phosphide (AlP) during the composite fabrication process. For the case of the phosphate A06 binder after heat treatment at 500 °C, the aluminium metaphosphate ($Al(PO_3)_3$) was the major phase, accompanied with the presence of the binder–whisker reaction product (silicon phosphate SiP_2O_7) and the binder–aluminium reaction product (aluminium phosphide AlP). For the case of the phosphate A23 binder after heat treatment at 500 or 800 °C, the binder–whisker reaction product (silicon phosphate SiP_2O_7) was the dominant phase, accompanied by the presence of the binder phase (aluminium metaphosphate $Al(PO_3)_3$) and the binder–aluminium reaction product (aluminium phosphide AlP).

The use of the phosphate A03, A06 and A23 binders all contributed to at least maintaining the tensile strength of the composite after heat exposure at 600 °C for 240 h. For all these binders, the binder phase was either $Al(PO_3)_3$ or $AlPO_4$. This suggests that aluminium metaphosphate ($Al(PO_3)_3$) or aluminium orthophosphate ($AlPO_4$) was responsible for the maintenance of the tensile strength of the composite after heat exposure at 600 °C for 240 h. The additional presence of silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) in the phosphate A06 and A23 (not A03) binder cases suggests that both silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) were responsible for the increase of the tensile strength of the composite before the heat exposure at 600 °C for 240 h and the further increase of the tensile strength of the composite after heat exposure at 600 °C for 240 h.

Comparison of the composites containing the preforms made by using the phosphate A06 and A23 binders after preform heat treatment at 500 °C for 4 h shows that (i) the higher the P/Al ratio, the larger the increase of the tensile strength before or after heat exposure at 600 °C for 240 h (Table III), and (ii) the

TABLE VIII Presence or absence of binder and reaction product phases in SiC whisker composites

Preform binder	Heat treatment (°C)	Binder phase $Al(PO_3)_3$ or $AlPO_4$	Reaction product SiP_2O_7	Reaction product AlP
Silica	500	–	–	–
Phosphate A03	500	⊕	–	+
Phosphate A03	1200 (argon)	⊕	–	–
Phosphate A06	500	⊕	+	+
Phosphate A23	500	+	⊕	+
Phosphate A23	800	+	⊕	+

+, Present; ⊕, present and dominant; –, absent.

higher the P/Al ratio, the greater the amount of silicon phosphate and stored phosphoric acid (or phosphorus in a certain form) (Table XI, Part II [2]). Therefore, the greater the amount of silicon phosphate and the stored phosphorus, the greater the increase of the tensile strength of the composite. In addition, the amount of aluminium phosphide was largest for the aluminium–binder–aluminium sandwich with the phosphate A23 binder (Table IV). Hence, the stored phosphorus in the phosphate A06 or A23 binder was responsible for supplying more reactant for forming silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) when the composite was heated at 600 °C for 240 h, thereby causing the composite to be strengthened by heating at 600 °C.

Comparison of Tables VIII and II shows that the composite with the preform made by using the phosphate A06 or A23 binders after heat treatment at either 500 or 800 °C possessed higher tensile strength than the composite containing the preform made by using the silica or the phosphate A03 binders after heat treatment at 500 °C in air or 1200 °C in argon. It is clear that the presence of the binder–whisker reaction product (silicon phosphate, SiP_2O_7) is the major contribution, especially when it was dominant. This means that the greater the amount of silicon phosphate, the higher the tensile strength of the composite. The presence of the binder–aluminium reaction product (aluminium phosphide, AlP) also contributed to the increase of the tensile strength of the composite. Owing to the minor amount of aluminium phosphide (AlP) in the composite containing the preform made by using the phosphate A03 binder after heat treatment at 500 °C, the strengthening effect of the aluminium phosphide (AlP) might be too small to increase the tensile strength of this composite. The absence of a strength increase for the composites containing the preform made by using the silica binder and that made by using the phosphate A03 binder after heat treatment at 500 °C in air or 1200 °C in argon shows that the binder phase (aluminium metaphosphate $Al(PO_3)_3$ or aluminium orthophosphate $AlPO_4$) did not increase the tensile strength of the composites. Comparison of the composites containing the preform made by using the phosphate A23 binder after heat treatment at 500 °C and after heat treatment at 800 °C (Table X, Part II [2]) shows that the composite with the preform heat treatment at 800 °C had a larger amount of silicon phosphate than that at 500 °C. However, the composite with the preform heat treatment at 800 °C showed a smaller increase of the tensile strength than that with the preform heat treatment at 500 °C (Table I). This is due to the excessive binder–whisker reaction (which damaged the SiC whiskers) for the preform after heat treatment at 800 °C, which was indicated by the lower tensile modulus of the composite containing the preform made by using the phosphate A23 binder after preform heat treatment at 800 °C than that after preform heat treatment at 200 or 500 °C (Table I). Although the excessive binder–whisker reaction degraded the SiC whiskers, the large amount of silicon phosphate was enough to provide a net increase in the tensile strength of the composite.

When the composites experienced heat exposure at 600 °C for 240 h, the composite containing the preform made by using the phosphate A03, A06 or A23 binders after preform heat treatment at 500 °C in air or 1200 °C in argon showed at least maintenance of the tensile strength (Table III). However, the composite containing the preform made by using the silica binder after composite heat exposure at 600 °C for 240 h showed a decrease of the tensile strength. A major difference between the composites containing the preforms made by using the silica and the phosphate binders was the presence of the aluminium metaphosphate ($Al(PO_3)_3$) or the aluminium orthophosphate ($AlPO_4$) in the latter (Table VIII). The tensile strength of the composites containing the preform made by using the phosphate A06 or A23 binder was further increased after heat exposure at 600 °C for 240 h. That the composite containing the preform made by using the phosphate A23 binder exhibited greatest increase in tensile strength after heat exposure at 600 °C for 240 h (Table III) and had more silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) compared to the composite made by using the phosphate A06 binder, indicates that the combination of the presence of the silicon phosphate (SiP_2O_7) and the aluminium phosphide (AlP) contributed to the further increase of the tensile strength of the composite after heat exposure at 600 °C for 240 h. The greater the amount of the silicon phosphate (SiP_2O_7) and the aluminium phosphide (AlP), the greater is the further increase of the tensile strength of the composite. Again, the small amount of aluminium phosphide (AlP) in the composite containing the preform made by using the phosphate A03 binder after heat treatment at 500 °C was insufficient to increase further the tensile strength of this composite.

The lower CTE for the composite containing the preform made by using the phosphate A23 binder compared to that made by using the silica binder is due to the better bonding strength between the whiskers and the aluminium matrix. This observation is consistent with the superior mechanical properties of the composites made by using the phosphate A23 binder. The difference in CTE was negligible at low temperatures, such as 35–100 °C, due to the low thermal stress at low temperatures. Therefore, both the composites (made by using the silica or the phosphate A23 binder) had enough bonding strength of the whiskers to withstand this low stress induced by the low thermal strain. However, at higher temperatures, the differences in CTE increased. The higher bonding strength of the whiskers in the composite containing the preform made by using the phosphate A23 binder (compared to that with the silica binder) reduced the thermal strain of the aluminium matrix near the SiC whiskers, thereby reducing the CTE of the composites. The better bonding strength was possible due to the reaction between the whiskers and the binders and that between the binder and aluminium. Silicon phosphate (SiP_2O_7) had been shown to be good for preparing a low CTE refractory [7].

Aluminium metaphosphate ($Al(PO_3)_3$) was reported to be a good high-temperature binder [8], at least up to 1000 °C. Above 1000 °C, it may dissociate to form aluminium orthophosphate ($AlPO_4$), which is not desirable [8] in terms of the binding strength. On the other hand, silicon phosphate (SiP_2O_7) does not volatilize or soften at temperatures up to 1650 °C [9]. In addition, silicon has a smaller ionic radius (Si^{4+}: 0.039 nm) [10] than Al^{3+} (0.050 nm), so that silicon phosphate is expected to have a higher binding strength than aluminium phosphate.

In conclusion, the binder phases (aluminium metaphosphate $Al(PO_3)_3$ or aluminium orthophosphate $AlPO_4$) protected the SiC whiskers from further attack by aluminium. This resulted in the maintenance of the tensile strength of the composites after heat exposure at 600 °C for 10 days. On the other hand, the reaction products (silicon phosphate SiP_2O_7 and aluminium phosphide AlP), which acted as *in situ* binders, enhanced the tensile strength of the composites before and after heat exposure at 600 °C for 10 days.

5.2. Role of the binders in carbon fibre composites

Comparing the mechanical properties of all carbon fibre composites (Table VI), it was found that the phosphate A23 binder was effective for giving the composite a relatively high tensile strength, even without the high-temperature heat treatment of the composite. An important factor that caused the higher tensile strength of the carbon fibre composite made by using the phosphate A23 binder (with either water or acetone as the vehicle) was the formation of the binder–aluminium reaction product (aluminium phosphide AlP) in the composite. In contrast, the carbon fibre composite containing the preform made by using the silica binder showed no reaction product (Fig. 5) to enhance the bonding strength of the carbon fibre in the aluminium matrix. Therefore, the coexistence of aluminium metaphosphate ($Al(PO_3)_3$) and aluminium phosphide (AlP) caused the composite containing the carbon fibre preform made by using the phosphate A23 binder (either with acetone or water) to have a higher tensile strength than that made by using the silica binder.

After the composite heat treatment at 600 °C for 2 or 14 h, the composite made by using the phosphate A23 binder with acetone (1:5) exhibited the best temperature resistance and the composite made by using the phosphate A23 binder with acetone (1:15) exhibited the second best temperature resistance (Table VII). From the binder content of the carbon fibre preform (Table III, Part II [2]) and the results of atomic absorption analysis (Tables XV–XVII, Part II [2], it is suggested that the greater the amount of phosphate A23 binder in the preform, the better the temperature resistance of the composite. This finding is consistent with the notion that the coexistence of aluminium metaphosphate ($Al(PO_3)_3$) and aluminium phosphide (AlP) helps the temperature resistance of the composite.

Carbon fibres tend to react with aluminium to form aluminium carbide (Al_4C_3), which is brittle and so undesirable for the composite [11]. The improvement of the temperature resistance of the composite containing the chopped carbon fibre preform made by using the phosphate A23 binder was probably due to the protection of the carbon fibres by the phosphate binder and the binder–aluminium reaction product, aluminium phosphide (AlP). The situation is similar to that for the SiC whisker composite except that there was no reaction between the carbon fibres and the phosphate binder. Therefore, the lack of a chemical reaction between the carbon fibres and the phosphate binder could be the reason for this composite to just maintain (but not increase) its tensile strength before and after heating at 600 °C for 2–14 h. Therefore, in general, the presence of the phosphate binder and aluminium phosphide (AlP) is not sufficient to enhance the tensile strength of the composites; the silicon phosphate phase is also required.

5.3. Comparison of new acid phosphate binder with commercial silica binder

Silica binder is widely used for the preparation of preforms for metal-matrix composites. However, the uneven distribution of the silica binder limits the machinability of the preform. The uneven binder distribution is indicated by the SEM observation of the surface and central parts of the preform made by using the silica binder after heat treatment at 200 °C. This observation is consistent with the large difference between the local compressive strengths of the surface part and the central part of the preform made by using the silica binder after heat treatment at 800 °C (Table VI, Part II [2]). It is also consistent with the lateral surface buckling failure mode in the compressive testing of the SiC whisker preform made by using the silica binder after heat treatment at 200, 500, 800 and 1100 °C. The difference in binder concentration between the surface and central parts of the preform made by using the silica binder was particularly large for the preform heat treatment at 1100 °C in air, as shown in the SiO_2 distribution obtained from XRD (Fig. 4, Part II [2]) and the SEM observation (Fig. 2, Part II [2]). However, this difference (though smaller) was also present for preforms heated at 200, 500 and 800 °C.

Instead of using the silica binder, the use of the acid phosphate binders leads to a more uniform binder distribution and hence better machinability. The more uniform binder distribution is suggested by the smaller difference in the local compressive strength between the surface and central parts of preforms made by using the phosphate A23 binder heat treated at 800 °C (Table VI, Part II [2]). It is also suggested by the shear failure mode of preforms made by using all phosphate binders. For preforms made by using the phosphate A23 binder heat treated at 1100 °C in air, XRD showed a much more uniform SiO_2 distribution than in preforms made by using the silica binder heat treated also at 1100 °C in air (Figs 4 and 8, Part II [2]). In addition to a more uniform binder distribution, the preforms made by using the phosphate binders were stronger under compression than those made by using the silica binder. Therefore, the preforms made by using the phosphate binders have better machinability, handlability and potential for near net-shape fabrication.

Owing to the non-reactivity of the silica binder with the SiC whiskers, the use of the silica binder is only for the purpose of holding the SiC whiskers together before metal infiltration. On the other hand, an acid phosphate binder not only holds the SiC whiskers together but also enhances the mechanical property and the temperature resistance of the resulting composite due to the reaction between the acid phosphate binder and the SiC whiskers. The reaction between the acid phosphate binders and the SiC whiskers forms silicon phosphate (SiP_2O_7), which enhances the bonding strength of the SiC whiskers. In addition to this, the reaction between the acid phosphate binder and the aluminium matrix forms aluminium phosphide (AlP), which also enhances the properties of Al/SiC_w and Al/C_f composites. The binder–aluminium reaction was not found for the case of the silica binder.

For the case of Al/C_f composites, the use of an acid phosphate binder gave better protection of the carbon fibres. The reaction between the acid phosphate binder and aluminium enhances the interface between the binder and aluminium, although this effect is not large, as it is overwhelmed by the more severe reaction between carbon fibres and aluminium. On the other hand, the silica binder gave no protection for the carbon fibres and no strengthening of the interface due to the uneven binder distribution and lack of the binder–aluminium reaction.

The main advantage of the new acid phosphate binder compared with the silica binder is that the reactivity of the acid phosphate binder with the SiC whiskers and aluminium resulted in the formation of *in situ* binders and hence increased the bonding strength of the whiskers. The lack of the reactivity of the silica binder with the SiC whiskers and aluminium resulted in no improvement of the bonding strength.

The use of the acid phosphate binders is expected to benefit other fillers, such as alumina and silicon nitride, due to the potential of reactions of the acid phosphate with these fillers to form aluminium phosphate and silicon phosphate, respectively. The reaction products are expected to act as *in situ* binders to enhance the mechanical properties of the preforms as well as the composites.

The use of the acid phosphate binder has a disadvantage, which is the release of the phosphorus (or phosphoric acid) during the preform heat treatment. This may produce an environmental problem and degrade the reliability of the heating equipment compared with the silica binder case.

5.4. Comparison of new acid phosphate binder with commercial phosphate MAP binder

The commercial phosphate MAP binder with a P/Al ratio of 3 is the same as the phosphate A03 binder, except that the former forms aluminium hydrogen phosphate ($AlH_2P_3O_{10}$) and the latter forms type C monoaluminium phosphate ($Al(H_2PO_4)_3$) after drying at 200 °C for 24 h. Both phosphate binders have no extra phosphoric acid (compared to the extra acid in the phosphate A06 and A23 binders) for forming silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) for enhancing the mechanical properties of the Al/SiC_w composites. The further increase of the tensile strength of the Al/SiC_w composites made by using the phosphate A06 and A23 binders after composite heat exposure at 600 °C for 240 h was not found for the composites made with the phosphate MAP and A03 binders. This is because the lack of the extra phosphoric acid in the phosphate MAP and A03 binders resulted in only the maintenance of the tensile strength of the Al/SiC_w composites after heat exposure at 600 °C for 240 h.

The Al/SiC_w composite made by using the phosphate MAP binder showed a slightly lower tensile strength, Young's modulus and ductility than the composite made by using the phosphate A03 binder, even though the binder weight fraction was essentially the same for both binders in the SiC whisker preforms (Table I, Part II [2]). This may be due to the presence of the visible impurity or other unknown impurity in the as-received commercial phosphate MAP binder, which was originally for large-volume applications in industry, such as painting or coating.

5.5. Effect of the P/Al ratio

The greater the amount of silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP), the greater the increase of the tensile strength of the Al/SiC_w composites. It was also shown that the formation of more silicon phosphate (SiP_2O_7) and aluminium phosphide (AlP) was due to the extra phosphorus stored in the binder. Table III, Part I [1], shows that the released phosphoric acid (H_3PO_4) increased as the P/Al atom ratio of the binder increased. Therefore, a P/Al ratio is associated with a larger phosphoric acid content and is favourable for the composite properties.

Although a higher P/Al ratio was desirable for the tensile strength of the Al/SiC$_w$ composite, it was not desirable for the tensile strength of the SiC whisker preforms (Table V, Part II [2]). This is due to the fact that the compressive strength of the preform is not only determined by the reactivity, which is governed by the P/Al ratio and the preform heat-treatment temperature, but is also determined by the binder concentration.

A higher P/Al ratio of the binder also benefits the properties of carbon fibre composites, due to the binder–aluminium reaction to form aluminium phosphide (AlP). However, a binder with a higher P/Al ratio may give a lower compressive strength of the carbon fibre preform due to the lack of the reactivity between the carbon fibres and the relatively small binder amount compared to that for a lower P/Al ratio.

5.6. Binder concentration

The binder concentration is mainly controlled by the amount of the carrier (such as water or acetone) added to the solution during preform fabrication by wet forming. The smaller the amount of the carrier added, the greater the amount of binder formed from drying at 200 °C. This was demonstrated by the comparison of the carbon fibre preform made by using the phosphate A23 binder with 1:15 acetone (more carrier) and that with 1:5 acetone (less carrier) (Table III, Part II [2]).

Another important factor which governs the binder concentration is the P/Al ratio. The higher the P/Al ratio, the greater the amount of extra phosphoric acid; the greater the amount of extra phosphoric acid, the lower the binder concentration due to the release of the phosphoric acid during heat treatment and the fact that aluminium metaphosphate itself has a P/Al ratio of only 3. This is true for both the binder by itself (Table III, Part I [1]) and the preform which used the binder (Table II, Part II [2]).

The effect of the binder concentration on the mechanical properties of the SiC whisker composite is not clear because the effect of the P/Al ratio (which resulted in the formation of silicon phosphate for cases with a high P/Al ratio) was dominant. On the other hand, the effect of the binder concentration on the temperature resistance of the carbon fibre composite was clearly demonstrated by the composites containing the preform made by using the phosphate A23 binder with 1:15 and 1:5 acetone carrier. The carbon fibre composite made by using the phosphate A23 binder with 1:5 acetone showed better temperature resistance due to its higher binder concentration, as shown by atomic absorption (Tables XVI and XVII, Part II [2]).

The preform heat-treatment condition also affects the binder concentration because the heat treatment drives off the extra phosphoric acid from the preform, resulting in a lower binder concentration. Therefore, the higher the heat-treatment temperature, the lower the resulting binder concentration in the preform.

5.7. Effect of the presence of SiC whiskers on the binder phases

In the presence of the SiC whiskers, the phosphate A03 and MAP binders formed a combination of type A and type B aluminium metaphosphate after heat treatment at 500 °C, in contrast to type B aluminium metaphosphate alone, for these binders by themselves. In the presence of the SiC whiskers, the phosphate A06 and A12 also formed a combination of type A and type B aluminium metaphosphate after heat treatment at 500 °C, in contrast to type A aluminium metaphosphate alone for these binders by themselves. Only the phosphate A23 binder had the same binder phase, namely type A aluminium metaphosphate, in the presence or absence of the SiC whiskers after heat treatment at 500 °C. After heat treatment at 800 °C, all the phosphate binders except MAP formed type A aluminium metaphosphate, in contrast to a combination of type B and A aluminium metaphosphate for the phosphate A03 and MAP binders by themselves. The phosphate MAP, in the presence or absence of the SiC whiskers, formed a combination of type A and type B aluminium metaphosphate. The changes of the binder phases in the presence of SiC whiskers was because the phase transformation condition was changed due to the presence of SiC whiskers.

For the phosphate A06 and A12 binders, the presence of the SiC whiskers raised the temperature of the transformation from type B to type A aluminium metaphosphate. On the other hand, for the phosphate A03 binder, the presence of SiC whiskers lowers this transformation temperature. Therefore, the presence of the SiC whiskers modified the transformation temperature for the type A aluminium metaphosphate.

6. Conclusion

The use of acid phosphate binders (prepared from $Al(OH)_3$ and phosphoric acid) instead of the widely used silica binder, resulted in improved tensile strength and temperature resistance of the Al/SiC$_w$ and Al/C$_f$ composites. The acid phosphate binders are expected to work well for SiC particles and graphite powder also. In general, they work best for siliceous fillers, such as Si_3N_4, SiO_2, Si, $MoSi_2$, etc., in aluminium and other metal matrices due to the formation of silicon phosphate (SiP_2O_7), which acts as an *in situ* binder and enhances the properties of the resulting composites. The acid phosphate binders are also expected to work, though less well, for non-siliceous fillers, such as Al_2O_3, MgO, TiO_2, AlN, TiB_2, C, etc., in aluminium due to the binder–aluminium reaction to form AlP. In the case of Al_2O_3 as the filler, phosphoric acid alone (without $Al(OH)_3$) can serve as the binder, because the reaction between Al_2O_3 and phosphoric acid forms extra aluminium metaphosphate or aluminium orthophosphate, which acts as an *in situ* binder. Thus, Al_2O_3 is expected to be a particularly suitable filler for the acid phosphate binders.

The uniformity of the binder distribution in preforms made using the phosphate binders enhances the mechanical properties of the preforms. This leads to better machinability of the preforms and higher potential for near net-shape fabrication.

Investigation of the effect of the P/Al atom ratio on the resulting properties of preforms containing siliceous materials had not been previously carried out. An increase in the P/Al atom ratio leads to an increase in the stored phosphoric acid (or phosphorus in other forms). The phosphoric acid (or phosphorus in other forms) was the active ingredient to form an *in situ* binder which helped the bonding strength. The understanding of this mechanism is useful for the design and use of acid phosphate binders for the binding of various materials.

Investigation of the effect of the preform heat-treatment conditions on the properties of Al/SiC_w had not been previously carried out. This work provided the optimum preform heat-treatment condition for enhancing the properties of the resulting Al/SiC_w composites.

Preforms made by using the acid phosphate binders and the heat-treatment procedure developed in this work are not only applicable to the liquid-metal infiltration technique, but also to squeeze casting.

The reaction between the acid phosphate binder and SiC forms silicon phosphate (SiP_2O_7). The reaction between the acid phosphate binder and aluminium forms aluminium phosphide (AlP). Both reaction products enhance the bonding strength of the SiC whiskers and lower the CTE of the SiC whisker composites. This understanding will be useful for future binder and composite material developments.

The degradation of Al/SiC composites upon heating due to the reaction between SiC and aluminium is a serious problem. This work provides a new method for improving the temperature resistance of Al/SiC. This method involves using an acid phosphate binder. Similarly, this method improves the temperature resistance of Al/C composites, which suffer from the reaction between carbon and aluminium, although the extent of improvement is less than in the case of Al/SiC. This method of thermal protection is much less expensive than coating the SiC or carbon filler with a barrier layer.

The scientific significance of this work is summarized below.

1. This is the first study of the relationships between preform preparation, preform properties and metal-matrix composite (MMC) properties. Preform preparation parameters include binder concentration in the slurry, binder composition, preform heat-treatment temperature and atmosphere. Preform properties affected include compressive strength and failure mode. MMC properties affected include tensile strength, yield strength, Young's modulus, ductility and CTE.
2. It is the first observation of binder-assisted SiC oxidation. Without a binder, no SiO_2 formation was observed for SiC whiskers heated at 1100 °C in air. With either silica or phosphate A23 binders, SiO_2 formation was observed, together with SiC whisker degradation.
3. The use of a binder–filler reaction product as an *in situ* binder is reported. This is desirable only when the reaction does not damage the filler excessively. Excessive damage occurred for phosphate A23 and silica binders heated at 1100 °C in air, which resulted in cristobalite SiO_2 due to SiC oxidation. When heated at $< 1100\,^{\circ}C$ in air, the phosphate A23 binder gave SiP_2O_7 as the binder–SiC reaction product, which was desirable.
4. A binder-matrix reaction product was used as an *in situ* binder.
5. The effect of the P/Al ratio of the acid phosphate binder on the preform and MMC properties was elucidated.
6. A binder (both *ex situ* and *in situ*) was used to improve the temperature resistance of an MMC for MMCs that suffer from filler–matrix reactions.
7. A binder was used to increase the strength of an MMC.
8. A binder was used to decrease the CTE of an MMC.
9. The effect of the SiC whiskers on the binder phases was elucidated.

The technological significance of this work is summarized below.

1. A new acid phosphate binder is reported for MMC (Al/SiC_w and Al/C_f) fabrication. The use of the acid phosphate binder was superior to that of the widely used silica binder for MMC fabrication.
2. A new method is described to increase the temperature resistance of MMCs.

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References

1. JENG-MAW CHIOU and D. D. L. CHUNG, *J. Mater. Sci.* **28** (1993) 1435.
2. *Idem, ibid.* **28** (1993) 1446.
3. JINGYU YANG and D. D. L. CHUNG, *ibid.* **24** (1989) 3605.
4. F. A. GIROT, J. M. QUENISSET and R. NASLAIN, *Compos. Sci. Technol.* **30** (1987) 155.
5. K. KANNIKESWARAN and R. Y. LIN, *J. Metals* **39**(9) (1987) 17.
6. T. W. CLYNE, M. G. BADER, G. R. CAPPLEMAN and R. A. HUBERT, *J. Mater. Sci.* **20** (1985) 85.
7. J. D. MORGAN, W. G. BJORKSTEDT and R. E. LOWE, US Pat. 1811 242, 23 June 1931, 5 December, 1985, 13pp.

8. C. TOY and O. J. WHITTEMORE, *Ceram. Int.* **15**(3) (1989) 167.
9. W. D. KINGERY, *J. Am. Ceram. Soc.* **33** (8) (1950) 239.
10. J. F. SHACKELFORD, "Introduction to Materials Science for Engineers" (Macmillan, 1985).
11. V. LAURENT, D. CHATAIN, N. EUSTATHOPOULOS and X. DUMANT, in "Proceedings of the International Symposium on Advances in Cast Reinforced Metal Composites", edited by S. G. FISHMAN and A. K. DHINGRA (1988) pp. 27–31.

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