The Effects of Binders and Heating Temperatures on the Properties of Preforms

J.-M. Chiou, B.-Y. Wei, and C.-M. Chen

The use of binders in fabricating ceramic fiber preforms is essential when producing metal-matrix composites via squeeze casting or liquid metal infiltration. The binder is not only used to stabilize the shape of the preform, but also to increase its strength. A strong preform is needed to make a net shape or near-net shape casting so that many post-machining processes can be reduced or eliminated. However, very little attention has been paid to preform fabrication, subsequent processing, and its characterization. This work focuses on the relation between preform processing (selection of binder, heat treatment of the preform, etc.) and the properties of the resulting preforms. Silica and phosphate binders were used to make short alumina fiber preforms. The use of binders and the heat treatments used were correlated to the properties of the resulting preforms. The results showed that the heat treating temperature, as well as the amount of binder, is relevant to the resulting properties of the preform. Correlations among the use of binders, heat treatment condition, composition of the binders, and the properties of the preforms were investigated.

Keywords

alumina fiber, compressive strength, heat treatment, metal matrix composite, phosphate binder, preform, silica binder

1. Introduction

RESEARCH on the fabrication of metal-matrix composites (MMC) has been extensive since the early 1980s.[1-5] This is because fabrication costs can be reduced by using emerging, less expensive processing techniques. Squeeze casting,[6,7] vacuum infiltration under pressure,[8-13] and die casting[14,15] are widely used for mass production.

A fibrous preform generally is required to produce a fiber-reinforced MMC through squeeze casting or metal infiltration. A preform is a porous media that is composed of fibers, whiskers, or particles. These fibers, whiskers, and particles act to improve the properties of the MMC. Properties that can be improved include Young's modulus, tensile strength, wear resistance, thermal expansion, etc.

Use of a binder generally is required to fabricate preforms. The binder not only stabilizes the shape of the preforms, but also increases its strength. Only when the preform has sufficient strength will it resist cracking or deformation during squeeze casting or metal infiltration.

A high-quality preform is essential for a high-quality resulting MMC. For example, if the fiber distribution is not uniform in a preform, variation in the properties of the resulting MMC may be significant, a serious consideration in commercial production. Binder content is another parameter that may affect the quality of preforms. If the binder content is not sufficient, the preform could be too weak to withstand the pressure of fabrication, resulting in deformation. On the other hand, if the binder content is too large, the excess binder, which always clusters at the surface of the preform,[12] could block the flow of the melt. The blockage causes an immediate increase in pressure during squeeze casting or metal infiltration, possibly resulting in deformation or cracking.

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1.1 *Literature Review*

Several papers[7,12,16,17] discuss the fabrication and characterization of preforms. Clyne et al. investigated MMC containing Saffil alumina fibers[7,16] and presented a model depicting deformation of the preform. The silica binder and a fugitive (latex) binding agent were used in their study. Friend et al. presented a process route for producing short-fiber/particulate hybrid MMCs by preform infiltration.[18] The preforms were produced by using a mixed binder consisting of silica and latex. Yang and Chung[10] manufactured a Fiberfrax HSA fiber-reinforced MMC using a silica binder. Fabrication and characterization of preforms was done by Chiou and Chung,[11-13] in which a new system of phosphate binders was used in fabricating SiC whisker preforms. They reported lower coefficients of thermal expansion and improved thermal resistance of the resulting MMCs compared to those of MMCs made using the silica binder.

For some applications that require only moderate tensile strength and the other well-known properties of MMCs, such as good wear resistance, high stiffness, low coefficients of thermal expansion and weight saving, a less expensive fiber can be used to reduce the fabrication cost. Therefore, Saffil alumina fibers were used in this study, because they are less expensive compared to whiskers, with good mechanical properties compared to aluminosilicate fibers. Phosphate binders were used, along with a silica binder for comparison, to study the effect of binders on the properties of the resulting Saffil preforms. The parameters considered in this study include the binder concentrations, heat treating time, and heat treating temperature.

1.2 *Phosphate Binders*

There are three methods of using phosphate bonding in refractories.[19] These include the use of (1) siliceous materials

with phosphoric acid, (2) oxides with phosphoric acid, and (3) direct addition or formation of an acid phosphate.

The acid phosphate used in method 3 is prepared by the addition of an acid (e.g., phosphoric acid) to a phosphate solution. The phosphoric acid acts as a bonding material. Generally, additions of aluminum, magnesium, iron, and beryllium greatly increase its bonding power.[19] These cations are all amphoteric or weakly basic and have moderately small atomic radii. In contrast, additions of calcium, barium, and thorium decrease bonding power. These cations are either highly basic or have large atomic radii. Optimum bonding is obtained only with weakly basic or amphoteric cations with moderately small atomic radii.[19] In addition to the chemical reactions of oxides with phosphoric acid, it was found that bonds may be formed by the loss of water from phosphoric acid or acidic phosphate solutions.

2. Experiments

2.1 *Preparation of Binders*

Two types of binders were used to prepare preforms. The first type was silica, which was used at a concentration of one part silica colloid (30 wt% silica in water) in various parts of water. The other type consisted of phosphates. Three different phosphate solutions were used in this study. The phosphate solutions were prepared by mixing one part of aluminum hydroxide—$Al(OH)_3$, obtained from E. Merck—with various parts of phosphoric acid (H_3PO_4, 85% GR grade, also obtained from E. Merck), so that these solutions had molar ratios, P/Al, of 3, 6, and 23.[20-22] For convenience, the corresponding phosphate binders were denoted A03, A06, and A23, respectively. After mixing the aluminum hydroxide, $Al(OH)_3$, and the phosphoric acid, H_3PO_4, the slurry was heated to around 150 °C while it was stirred. It was held at ~150 °C until all of the solids were dissolved. All of the phosphate binders were made at concentrations of one part of phosphate solution in 5, 10, 15, or 40 parts of water, denoted 1:5, 1:10, 1:15, or 1:40, respectively.

2.2 *Fabrication of Preforms*

Fabrication of the Saffil fiber preforms was achieved by wet forming. After making a slurry by mixing Saffil fibers with the binder, wet forming was performed using a hydraulic press at a pressure (<10 kPa for 6.5 vol% and <3 MPa for 20 vol%) that was sufficient to obtain the required volume fraction. Drying of the preforms was carried out in air at 200 °C for 24 h.

2.3 *Heat Treatment of Preforms*

Two different types of Saffil preforms were fabricated in this study. The first type was a Saffil preform with a volume fraction of 6.5%. The effects of heat treatment temperature or time on binder contents and compressive strengths of preforms were studied for this type. Each set of preforms of this type was dried at 200 °C, then heated at a higher temperature for several different lengths of time. A minimum of three samples were made for each condition.

Drying of the binder in the preforms was complete after heating at 200 °C for 24 h. Three different temperatures—500, 800, and 1000 °C—were used for heat treating the preforms after drying. The temperature was increased from room temperature at the rate of 10 °C/min, kept at the target temperature (500, 800, or 1000 °C) for 4 h, and then cooled to room temperature at the rate initially of 10 °C/min and finally (below around 600 °C) at a rate corresponding to furnace cooling (i.e., cooling rate of <10 °C/min).

The second type of preform was a Saffil preform with a volume fraction of 20%. Due to the minimal effect of time on the 6.5 vol% preforms (see Section 3.1.1.1), only the effect of heat treating temperature was studied for the 20 vol% preforms.

Because there was minor surface cracking in the 20 vol%, rather than 6.5 vol%, preforms made with phosphate A06 and A23 binders, an experiment was done to study the effect of heating rate on cracking. The result show that, for 20 vol% Saffil preforms, a low heating rate (such as 1 °C/min) easily causes surface cracking. On the other hand, a high heating rate (such as ~10^4 °C/min) produces better results. Therefore, the 20 vol% Saffil preforms were not dried first, but heated directly at the target temperature for a designated time (39 h for 200 °C and 6 h for 500 and 800 °C). This process does not include any ramp stage. Preforms heat treated as described above are hereafter denoted as Saffil (20 vol%)/200 °C, Saffil (20 vol%)/500 °C, and Saffil (20 vol%)/800 °C, respectively. The superior results obtained for the Saffil (20 vol%) preform heat treated at a higher heating rate could be because the high reaction rate of the binder allowed sufficient time to enhance the binding strength at the preform surface before the occurrence of springback action from the center portion of the preform. Springback action is probably due to the loss of surface tension of the binder solution on heating, which maintains the newly formed preform shape.

3. Results

3.1 *Binder Content of Preforms*

3.1.1 6.5 Vol% Saffil Preforms

3.1.1.1 *Effect of Heat Treating Time on Drying*

Binder content is obtained from dividing the weight gain of the preform after drying by the original weight of the fibers before incorporation into the fabrication process. Table 1 shows the binder contents of the 6.5 vol% Saffil preforms fabricated by using the phosphate A06 and A23 binders, both at the concentration of 1:10. These preforms were dried at 200 °C in an "intermittent heating" process. That is, during the 24-h drying

Table 1 Binder contents of Saffil (6.5 vol%)/A06 (1:10) and A23 (1:10) after drying at 200 °C

Heating time, h	Binder content, % A06 (1:10)	A23 (1:10)
1	32.6 ± 2.9	31.2 ± 1.5
2	32.3 ± 2.2	29.6 ± 1.2
4	32.2 ± 2.1	29.5 ± 1.2
8	31.5 ± 2.1	...
24	31.2 ± 2.1	29.2 ± 1.4

period, preforms in the same group were moved from the furnace, weighed, and then put back in the furnace for further heating at the designated time (such as at 1, 2, 4, or 8 h). According to the results, the preform was mostly dry after heating for several hours. After 24 h, the variation in binder content was relatively small compared to its standard deviation. Therefore, in this study, the preforms were assumed dried after heating at 200 °C for 24 h.

3.1.1.2 *Effect of Heat Treating Temperature*

All of the 6.5 vol% Saffil preforms were dried at 200 °C and then heat treated to the specified higher temperature. Table 2 shows the binder contents of the 6.5 vol% of Saffil preforms made with silica (1:10 and 1:5), phosphate A06 (1:40 and 1:10), and phosphate A23 (1:40 and 1:10) binders. These preforms were dried at 200 °C or further heat treated up to 500, 800, or 1000 °C for 4 h. At least 9, and up to 15, samples were tested for each condition. The results show that the binder content of the preforms made with the same binder concentration decreases as the heat treating temperature increases, with one exception—A06 (1:40)/1000 °C. On further examination, one finds that the standard deviations are somewhat higher compared to variations in the binder contents due to changes in heating temperatures. This is probably due to the uneven segregation of binders in preforms. Figure 1 shows scanning electron microscope (SEM) photographs of the surface and center of Saffil (6.5 vol%)/A06 (1:10)/500 °C. Note that the binder was much more abundant on the surface than in the center.

Comparing the standard deviations among the preforms made with phosphate A23 (1:40 or 1:10) binders and preforms made with phosphate A06 (1:40 or 1:10) binders, one finds that the preforms made with phosphate A06 (1:10) binder have larger standard deviations. This could be due to the higher concentration of PO_4^{3-} or PO_3^-, which could form more binder phase, $Al(PO_3)_3$ or $AlPO_4$ (see Section 4.3), in phosphate A06 binder than in phosphate A23 binder. This effect becomes less significant when the resulting binder content is lower (e.g., 1:40).

3.1.1.3 *Effect of Binder Concentration*

Table 2 also shows that the binder content of a preform increases as the binder concentration increases. In other words, a higher binder concentration means that less water is added to the binder solution and results in a higher binder content of the preform. For example, the binder content of the preforms made with phosphate A23 (1:10) (higher concentration) binder is higher than that of the preform made with phosphate A23 (1:40) (lower concentration).

3.1.2 20 Vol% Saffil Preforms

3.1.2.1 *Effect of Drying at Room Temperature*

Because silica and phosphates are different binders, they have different binding mechanisms. Silica binder gains its binding power through the coalescence of silica particles on the loss of water.[23] However, phosphate binders rely primarily on

Table 2 Binder contents of Saffil (6.5 vol%) preforms after heat treatment

Heating temperature, °C	Binder content, %					
	Silica (1:10)	Silica (1:5)	A23 (1:40)	A23 (1:10)	A06 (1:40)	A06 (1:10)
200	9.09 ± 1.12	15.82 ± 1.17	7.53 ± 0.21	29.33 ± 1.23	10.25 ± 0.75	31.92 ± 2.81
500	8.29 ± 1.09	15.65 ± 2.77	5.96 ± 0.54	...	5.81 ± 0.27	27.35 ± 5.87
800	8.14 ± 1.43	15.93 ± 1.23	5.60 ± 0.34	26.17 ± 0.97	5.76 ± 0.70	25.11 ± 5.98
1000	8.01 ± 0.86	...	5.56 ± 0.51	25.19 ± 1.36	6.11 ± 0.54	24.02 ± 5.31

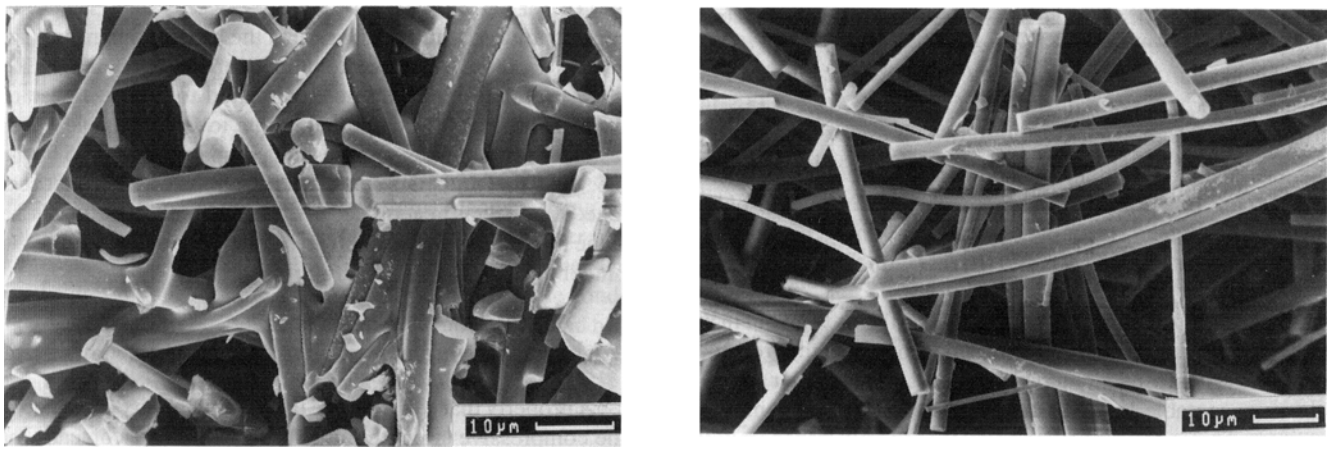


Fig. 1 SEM photographs of the surface (a) and center (b) of Saffil (6.5 vol%)/A06 (1:10)/500 °C preforms.

Table 3 Binder contents of Saffil (20 vol%) preforms after heat treatment at 500 °C for 6 h

Binder concentration	Binder content, %			
	SiO_2 (500 °C)	A03 (500 °C)	A06 (500 °C)	A23 (500 °C)
1:5	4.6 ± 0.9	17.4 ± 0.3	15.2 ± 0.5	14.7 ± 0.2
1:10	3.0 ± 0.4	7.2 ± 0.2	7.7 ± 0.7	7.1 ± 0.5
1:15	1.4 ± 0.7	5.1 ± 0.1	3.8 ± 0.5	4.5 ± 0.1

Table 4 Binder contents of Saffil (20 vol%) preforms with a binder concentration of 1:10

Heating temperature, °C	Binder content, %			
	SiO_2 (1:10)	A03 (1:10)	A06 (1:10)	A23 (1:10)
200	3.4 ± 0.2	6.9 ± 0.2	7.5 ± 0.2	7.2 ± 0.2
500	3.0 ± 0.4	7.2 ± 0.2	7.7 ± 0.7	7.1 ± 0.5
800	3.0 ± 0.1	...	7.4 ± 0.3	6.7 ± 0.1

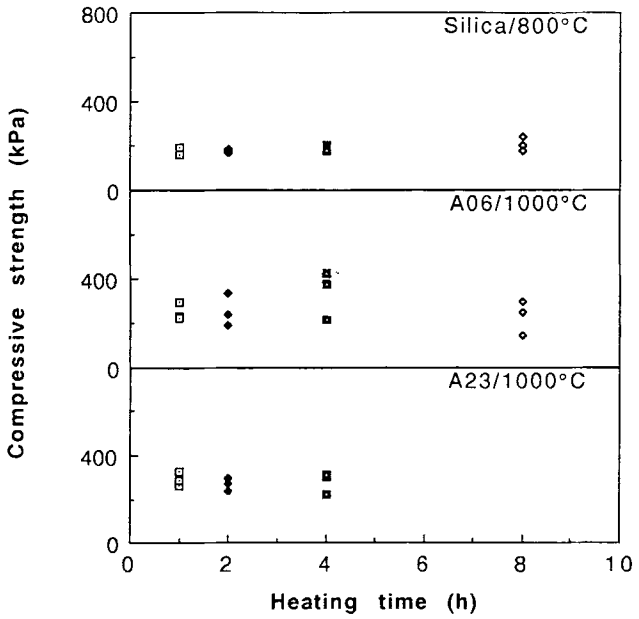


Fig. 2 Compressive strength of 6.5 vol% Saffil preforms made using the silica (1:5), A06 (1:10), and A23 (1:10) binders and after heat treatment at 800 or 1000 °C for different times.

chemical reactions with the Saffil fibers and secondarily on the dehydration of the binder itself.[19] Therefore, diluted phosphate binders (1:15, 1:20, or 1:30) normally need higher temperatures (such as 200 or 500 °C) to react with the Saffil fiber to form a bond.

Accordingly, if the newly fabricated preforms were put in an open environment, such as an air conditioned room, preforms made with silica binder could keep almost all the binder and obtain an acceptable level of strength when dried at room temperature. This is because silica particles can only transport with water to the surface of preforms and can not float en masse into the air. However, for preforms made with phosphate binders, the diluted phosphate solution would be drawn out by the vaporized water into the air before the occurrence of the required chemical reaction. This effect would cause the loss of binder in the preform and would result in weak strength levels in the preforms. The above derivation was confirmed by an experiment in which almost zero binder content was obtained by putting three sets of newly formed preforms, namely Saffil (20 vol%)/A06 (1:15), Saffil (20 vol%)/A06 (1:20), and Saffil (20 vol%)/A06 (1:30), in an air-conditioned room for 5 days.

3.1.2.2 *Effect of Binder Concentration*

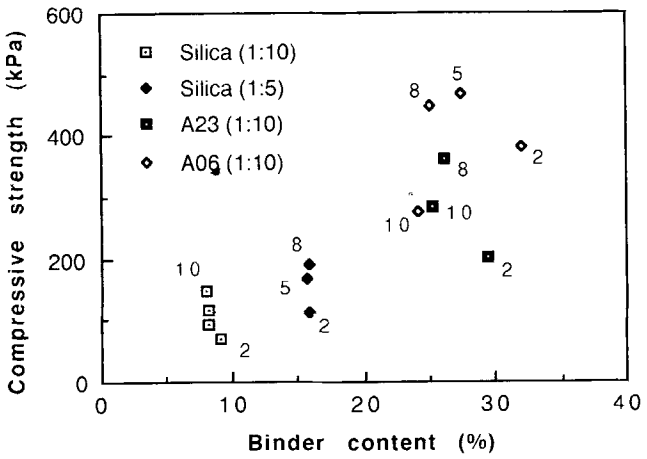
Table 3 shows the binder contents of the Saffil (20 vol%) preforms made with binder concentrations of 1:5, 1:10, and 1:15 and heat treated at 500 °C for 6 h. It clearly shows that the binder content increases as the binder concentration increases. The comparatively lower binder content of the preforms made with silica binder is because the original silica colloids already contain 70% water, which actually increases the amount of the water added and decreases the actual binder concentration.

3.1.2.3 *Effect of Heat Treating Temperature*

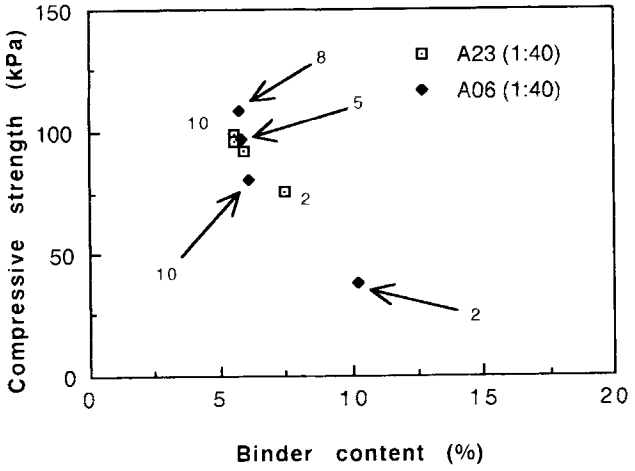
Table 4 shows that the binder contents of the Saffil (20 vol%)/(1:10) preforms after heat treatment at 200 °C for 39 h, 500 °C for 6 h, and 800 °C for 6 h. With only three samples in each condition, results indicate that the binder content does not always decrease as the heat treating temperature increases. The more profound inconsistency, compared to its counterpart of the Saffil (6.5 vol%), is probably due to fewer samples being tested. Three samples were tested, compared to 9 to 15 for the 6.5 vol% preform. The standard deviations of the binder contents of preforms heat treated at different temperatures with the same binder content were always greater than the variations in binder content due to temperature change.

3.2 *Compressive Strengths of Preforms*

A property that can describe the binding ability of a binder is the compressive strength of the preform. Microscopically, the individual Saffil fibers intersect one another with the aid of the binder to form a three-dimensional network. Because the binder is weak compared to the fibers, under compression, the preform will fail at the binder rather than at the fibers.



(a)



(b)

Fig. 3 Compressive strength versus binder content and heat treating temperature for (a) preforms of Saffil (6.5 vol%)/silica (1:10), Saffil (6.5 vol%)/silica (1:5), Saffil (6.5 vol%)/A06 (1:10), and Saffil (6.5 vol%)/A23 (1:10); and (b) preforms of Saffil (6.5 vol%)/A06 (1:40) and Saffil (6.5 vol%)/A23 (1:40).

3.2.1 6.5 Vol% Saffil Preforms

3.2.1.1 *Effect of Heat Treating Time*

Figure 2 shows the compressive strengths of 6.5 vol% Saffil preforms (25 mm diameter, 25 mm height) made by using the SiO_2 (1:5), A06 (1:10), and A23 (1:10) binders and after heat treatment at 800 or 1000 °C for different lengths of time. The scatter in compressive strengths of preforms at the same condition of processing (binder, heat treatment temperature, and heat treating time) are greater than variations in the compressive strengths of preforms due to a change in heat treatment.

3.2.1.2 *Effect of Heat Treating Temperature*

Figure 3 illustrates the relationship between compressive strength and heating temperature for preforms of Saffil (6.5 vol%)/SiO_2 (1:5), Saffil (6.5 vol%)/SiO_2 (1:10), Saffil (6.5 vol%)/A06 (1:10), Saffil (6.5 vol%)/A23 (1:10), Saffil (6.5 vol%)/A06 (1:40), and Saffil (6.5 vol%)/A23 (1:40). The values 2, 5, 8, and 10 in the figure represent 200, 500, 800, and 1000 °C, respectively. The compressive strength of the preforms of both Saffil (6.5 vol%)/silica (1:10) and Saffil (6.5 vol%)/silica (1:5) increases as the heat treating temperature increases. For the preform of Saffil (6.5 vol%)/A06 (1:10 and 1:40), Fig. 3 shows that the compressive strengths of preforms heat treated at 500 and 800 °C are higher than those heat treated at 200 and 1000 °C. For the preform of Saffil (6.5 vol%)/A23 (1:10), Fig. 3 shows that the compressive strengths of preforms heat treated at 800 °C is highest, those heat treated at 1000 °C have the next highest strength, and those heat treated at 200 °C the lowest. However, for the preform of Saffil (6.5 vol%)/A23 (1:40), Fig. 3 shows that the higher the heat treating temperature, the greater the compressive strength. The above results reveal that, in addition to binder content, the compressive strength of a preform also depends on heat treating temperature.

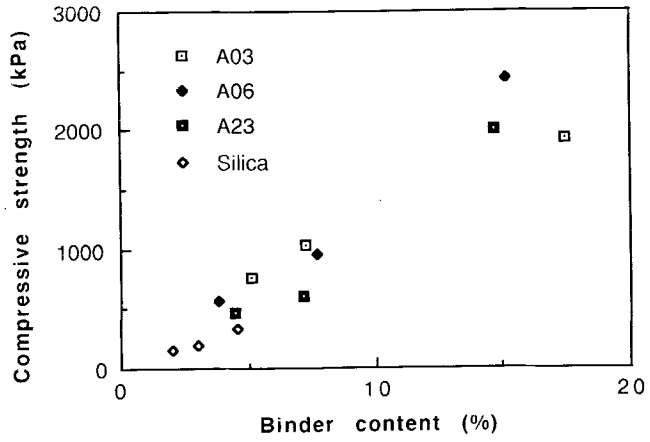


Fig. 4 Compressive strength versus binder content for Saffil (20 vol%)/500 °C preforms.

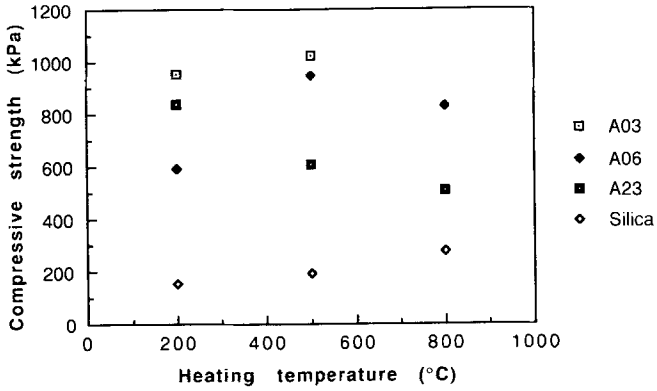


Fig. 5 Compressive strength versus heat treating temperature for Saffil (20 vol%)/(1:10) preforms.

3.2.2 20 Vol% Saffil Preforms

3.2.2.1 *Effect of Binder Content*

Figure 4 shows that the relationship between compressive strength and binder content of the 20 vol% Saffil preforms heat

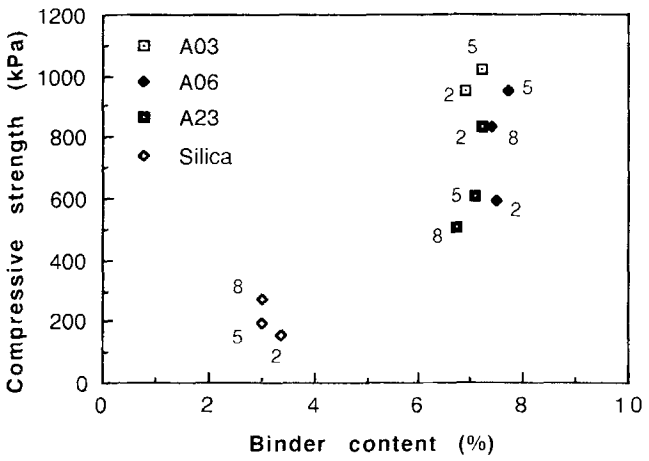


Fig. 6 Compressive strength versus binder content and heat treating temperature for Saffil (20 vol%) preforms.

treated at 500 °C for 6 h. Note that the compressive strength increases as the binder content increases. When the binder content is less than 10%, the Saffil (20 vol%)/A03 has the highest compressive strength, the Saffil (20 vol%)/A06 the second, the Saffil (20 vol%)/A23 the third, and the Saffil (20 vol%)/SiO_2 the lowest. However, when binder content is greater than 10%, the compressive strength of Saffil (20 vol%)/A03 is unusually low compared to the other two preforms.

3.2.2.2 *Effect of Heat Treating Temperature*

Figure 5 shows the compressive strength of Saffil (20 vol%)/(1:10) preforms in terms of heat treating temperature. Note that (see Table 4) all of the preforms made with phosphate binders have similar binder contents and that preforms with silica binder have less than half the amount of binder content than preforms made with phosphate binders. The compressive strength of the Saffil (20 vol%)/SiO_2 (1:10), versus its counterpart of 6.5 vol%, increases as the heat treating temperature increases. Saffil (20 vol%)/A03 (1:10) exhibits a similar trend, but with only two heat treating temperatures. On the other hand, the compressive strength of Saffil (20 vol%)/A06 (1:10) reaches an optimum value when heat treated at 500 °C and decreases somewhat at 800 °C. Furthermore, the compressive strength of Saffil (20 vol%)/A23 peaks when heat treated at 200 °C and then decreases as the heat treating temperature increases. Figure 6 shows the compressive strengths of preforms with a variation in binder content. The values 2, 5, and 8 represent 200, 500, and 800 °C, respectively. When the binder content of the preforms is similar, the heat treating temperatures are dominant.

3.3 *Reaction between Binders and Saffil Fibers*

A study of the reaction between the Saffil fibers and the binders was performed by making blocks of Saffil fibers with undiluted silica or phosphate solutions (without any water addition). The binders were used at the concentration of one part of silica without water or one part of phosphate solution without water. Although the absence of water was in contrast to the actual conditions used in preparing the preform, it rendered the binder/fiber reaction experimentally more observable, because the binder concentration was higher in the Saffil fiber blocks than in the Saffil preforms.[12]

Table 5 Crystalline phases of Saffil blocks after heat treatment (a)

Block	200 °C	500 °C	800 °C
Saffil/silica (1:0) ...	Amorphous	Amorphous	Amorphous SiO_2 (Cristobalite)(b)
Saffil/A03 (1:0).....	$AlPO_4$ (Berlinite) $AlH_2P_3O_{10}$(b)	$Al(PO_3)_3$ (B) $AlPO_4$ (Berlinite) $AlPO_4$ (31-28)	$Al(PO_3)_3$ (B) $AlPO_4$ (Berlinite) $Al(PO_3)_3$ (A) $AlPO_4$ (31-28)
Saffil/A06 (1:0).....	Amorphous	$Al(PO_3)_3$ (B) $AlPO_4$ (31-28)	$Al(PO_3)_3$ (B) $AlPO_4$ (31-28) $Al(PO_3)_3$ (A) $AlPO_4$ (Berlinite)
Saffil/A23 (1:0).....	Amorphous	$Al(PO_3)_3$ (B) $AlPO_4$ (31-28)	$Al(PO_3)_3$ (B) $AlPO_4$ (31-28)

Note: $Al(PO_3)_3$ (A) represents the crystal in form A, and $Al(PO_3)_3$ (B) represents form B, according to the Powder Diffraction File/Inorganic, published by JCPDS, PA, USA, 1982. (31-28) represents the card file no. of the crystal, from the same source. (a) Phases from the Saffil fibers are excluded. (b) The phase is assumed based on several of the strongest peaks.

Table 6 Crystalline phases of binders after heat treatment[11]

Binder	200 °C	500 °C	800 °C
Silica	Amorphous	Amorphous	SiO_2 (Cristobalite)
A03	$AlPO_4$ (Berlinite)	$Al(PO_3)_3$ (B)	$Al(PO_3)_3$ (B) $Al(PO_3)_3$ (A)
A06	Amorphous	$Al(PO_3)_3$ (B)	$Al(PO_3)_3$ (A)
A23	Amorphous	$Al(PO_3)_3$ (A)	$Al(PO_3)_3$ (A)

After drying at 200 °C for a week, the blocks were heat treated at 500 and 800 °C for 4 h, as during preform preparation. X-ray diffraction was performed to characterize the crystalline phases of the Saffil blocks. Table 5 summarizes the crystalline phases, except those of the Saffil fibers, for the Saffil blocks after heat treatments. Crystallization phases changed as the heat treating temperature varied. Table 6[11] gives the crystalline phases of the binders, themselves heat treated under the same conditions. Comparing Tables 5 and 6, one finds that no new crystalline phases emerged when silica was used in the Saffil block and heat treated up to 800 °C. On the other hand, the phosphate solutions experienced phase changes when used in the Saffil blocks. This is partly due to the chemical reactions between the phosphate solutions and Al_2O_3 in the Saffil fibers[19] and probably partly due to variations in the P/Al ratio[20-21] caused by introduction of Saffil fibers.

4. Discussion

4.1 *Effect of Volume Fraction on Binder Content*

The higher the binder concentration, the less water needed to dilute the binder solution. Therefore, the fact that binder content increases as binder concentration increases was anticipated and was observed. However, with the same binder

Table 7 Effect of binder on the compressive strength of Saffil (6.5 vol%) / (1:10) preforms

	200 °C	500 °C	800 °C	1000 °C
A06 (1:10)				
Strength (a)	30	43	45	30
ex situ binder	24	24	24	24
in situ binder	6	19	21	6
A23 (1:10)				
Strength	16	...	35	28
ex situ binder	8	...	8	8
in situ binder	8	...	27	20

(a) Strengths were obtained by normalizing the compressive strengths with the binder content at 25 wt% and scaling to simple numbers.

Table 8 Effect of binder on compressive strength of Saffil (6.5 vol%) / (1:40) preforms

	200 °C	500 °C	800 °C	1000 °C
A06 (1:40)				
Strength (a)	3	10	11	8
ex situ binder	3	6	6	6
in situ binder	0	4	5	2
A23 (1:40)				
Strength	6	9	9.5	10
ex situ binder	2	2	2	2
in situ binder	4	7	7.5	8

(a) Strengths were obtained by normalizing the compressive strengths with the binder content at 6 wt% and scaling to simple numbers.

concentration, for example 1:10, Saffil (6.5 vol%) had a much higher binder content (Table 2) than Saffil (20 vol%) (Table 3).

This phenomenon becomes clear if the definition of binder content is reviewed. Binder content is obtained by dividing the weight gain due to the use of binder by the weight of fibers originally used. For a constant volume, Saffil (20 vol%) has about three times the weight of Saffil (6.5 vol%), e.g., 30 g compared to 10 g. The same weight of binder will result in different binder contents for different volume fractions. For example, 3 g of binder is a binder content of 30% to a 10-g Saffil (6.5 vol%), but only a binder content of 10% to Saffil (20 vol%). The binder content obtained in this study was about 27% for the Saffil (6.5 vol%)/A06 (1:10)/500 °C and about 8% for Saffil (20 vol%)/A06 (1:10)/500 °C. The ratio of the binder content (27:8) is close to the ratio of 3.

4.2 *Compressive Strength*

The compressive strength of preforms is primarily due to the binding effect of the binder used. An effort was made to clarify all of the phenomena observed in this study. However, the results of compressive strength comparisons were very complicated in terms of binder type, binder content, heat treating temperature, and heat treating process, particularly when phosphate binders were used for binding alumina Saffil fibers. Table 6 shows that phosphate binders only formed $Al(PO_3)_3$ or $Al(H_2PO_4)_3(C)$ after heat treatment. Table 5 shows that, in the presence of Saffil fibers, they formed $Al(PO_3)_3$, $AlPO_4$, and/or $AlH_2P_3O_{10}$ after heat treatment. However, from the fundamentals of phosphate bonding (Section 1.2),[19] the phosphoric acid in the phosphate binders could react with Al_2O_3 to form either $AlPO_4$ or $Al(PO_3)_3$ phases. From comparison of Tables 5 and 6, no apparent method can be used to tell whether it is a reaction product. This creates more difficulties in analyzing binder effects. Therefore, the use of the terms *ex situ* and *in situ* binders is proposed.

Table 9 Effect of binder on the compressive strength of Saffil (20 vol%) / (1:10) preforms

	200 °C	500 °C	800 °C
A03 (1:10)			
Strength (a)	9	10	...
ex situ binder	6	6	...
in situ binder	3	4	...
A06 (1:10)			
Strength	6	9	8
ex situ binder	3	3	3
in situ binder	3	6	5
A23 (1:10)			
Strength	8	6	5
ex situ binder	1	1	1
in situ binder	7	5	4

(a) Strengths were obtained by normalizing the compressive strengths with the binder content at 7 wt% and scaling to simple numbers.

4.3 *Ex situ and in situ Binders*

The use of phosphate binders for fabricating Saffil preforms is commonplace (see method 3 in Section 1.2). The phosphate solutions used for Saffil preforms essentially consist of two types of binding phases. One is the phases formed due to the loss of water, or chemical reactions within the binder solution itself. The other is the phases due to the chemical reaction between the binder solution and the Saffil fibers. Accordingly, the former is classified as an *ex situ* binder and the latter as an *in situ* binder.

The *ex situ* binder can be identified from the phase(s) of the binder itself after heating to higher temperatures (see Table 6). Table 6 shows that generally a P/Al ratio of 3 is required for these phases to form. If the same amount of binder solution is used, the molar ratio of aluminum in each binder solution is calculated as A03:A06:A23 = 6.3:3.5:1. Because the ratios of P/Al are all larger than or equal to 3 for these phosphate solutions, the formation of an *ex situ* binder, in terms of aluminum metaphosphate ($Al(PO_3)_3$), is determined by the amount of aluminum. Therefore, the ratio of the amount of *ex situ* binder would be roughly A03:A06:A23 = 6:3:1.

On the other hand, the chemical reaction between the binders and the Saffil fibers is due to the existing phosphoric acid, which reacts with the alumina Saffil fibers. The higher the ratio of P/Al, the more phosphoric acid is present in the binder solution. Because the phosphoric acid is the only reactive agent in the phosphate binder, the reactivity of the phosphate binder is directly related to the concentration of the phosphoric acid. Therefore, the phosphate A23 binder, with P/Al = 23, has the highest reactivity and the phosphate A06 binder the second.

For the silica binder, no apparent reaction product was found. Table 6 indicates that there is practically no reactivity for silica binder with Saffil fibers. Therefore, the preform made with the silica binder consists of only *ex situ* binder.

4.4 *Effect of Heat Treating Temperature*

4.4.1 Effectiveness of ex situ and in situ Binders

Table 7 shows the effect of binders in terms of the effectiveness of *ex situ* and *in situ* binders on the compressive strength of Saffil (6.5 vol%)/(1:10) preforms. Strengths were obtained by normalizing the binding content at 25% from Fig. 3 and scaling to simple numbers. Table 8 shows the binder effect on the compressive strength of Saffil (6.5 vol%)/(1:40) preforms. Strengths were obtained by normalizing the binder content at 6% also from Fig. 3 and scaling to simple numbers. Table 9 shows the effect of binders on the compressive strength of Saffil (20 vol%)/(1:10) preforms. The strengths were obtained by normalizing the binder content at 7% from Fig. 4 and scaling to simple numbers. The effectiveness of the *ex situ* binder was assumed to be around 30 to 60% of the overall binding effect for phosphate A06. The values demonstrate the relative change in effectiveness of the *in situ* binder due to the change in heat treating temperature. They do not represent any absolute physical quantity. The effectiveness of phosphate A03 and A23 binders was determined according to the ratio of the *ex situ* binder contained in each phosphate binder, i.e., A03:A06:A23 = 6:3:1, which was described in Section 4.3. The change in the effectiveness of the *ex situ* binder on heating was assumed to be negligible, because the effect of the change in crystalline phases on strength is relatively minor compared to the effect of binder content.[12] Therefore, the effectiveness of the *ex situ* binder was determined to be same at all temperatures. The effectiveness of the *in situ* binder was determined by subtracting the value of the strength by the effectiveness of the *ex situ* binder.

4.4.2 Maximum Compressive Strength and Optimal Heat Treating Temperature

Tables 7 to 9 show that the effectiveness of the *in situ* binder increases as the heat treating temperature increases up to a maximum temperature and strength peak and then decreases as the heat treating temperature increases further. A heat treating temperature that allows a system of preform/binder to reach its maximum compressive strength is called the optimal heat treating temperature for that system. By this definition, the maximum compressive strength is always accompanied by the optimal heat treating temperature and the maximum effectiveness of the *in situ* binder. From Table 7, the optimal heat treating temperatures for the Saffil (6.5 vol%)/A06 (1:10) and Saffil (6.5 vol%)/A23 (1:10) are both 800 °C. From Table 8, the optimal heat treating temperatures for the Saffil (6.5 vol%)/A06 (1:40) and Saffil (6.5 vol%)/A23 (1:40) are 800 and 1000 °C, respectively. On the other hand, from Table 9, the optimal heat treating temperatures for the Saffil (20 vol%)/A03 (1:10), Saffil (20 vol%)/A06 (1:10), and Saffil (20 vol%)/A23 (1:10) are 500, 500, and 200 °C, respectively. Additionally, as shown in Fig. 3, the optimal heat treating temperatures for the Saffil (6.5 vol%)/silica (1:5) and Saffil (6.5 vol%)/silica (1:10) are both 1000 °C.

When the actual heat treating temperature is lower than the optimal heat treating temperature, the increasing effectiveness of the *in situ* binder is due to the more intense chemical reaction that occurs on heating. The higher the heating temperature, the greater the chemical reaction. However, when the heating temperature is too high, an excessive chemical reaction may occur and degrade the fibers, which results in lower compressive strength of the associated preform and a decrease in the effectiveness of the *in situ* binder. Consequently, when the heat treating temperature is higher than the optimal heat treating temperature, the decreasing effectiveness of *in situ* binder is due to too great a reaction. Again, the higher the heat treating temperature, the greater the decrease in effectiveness of the *in situ* binder. Thus, determination of the maximum compressive strength depends on the optimum combination of effectiveness of the *ex situ* and *in situ* binders. Generally, the optimum effectiveness of the *in situ* binder depends on the heat treating temperature. Therefore, the maximum compressive strength depends on selection of the optimum heat treating temperature.

The same rule also applies to preforms made with silica binder. Due to the nonreactivity of silica binder with the Saffil fibers at temperatures below 1000 °C, only the *ex situ* binder exists after heat treatment. Therefore, heat treatment at a higher temperature leads to a higher binding effectiveness, even though the effect is not significant. Hence, preforms made with silica binder reached their maximum compressive strength at 1000 °C.

4.4.3 Effect of Binder Content on Optimal Heat Treating Temperature

By comparing Tables 7 and 8, one finds that the optimal heat treating temperature of the Saffil (6.5 vol%)/(1:40) was higher than (such as A23) or equal to (such as A06) that of the Saffil (6.5 vol%)/(1:10) preform. It indicates that, as the binder content is higher (as 1:10), the optimal heat treating temperature tends to be lower. This could be due to the fact that the higher binder content contains more H_3PO_4 relative to the fibers, leading to a higher reaction rate. The higher reaction rate results in the occurrence of an earlier over-reaction. Hence, the optimal heat treating temperature is lower.

4.4.4 Effect of Heat Treating Process on Optimal Heat Treating Temperature

The heat treating process for the Saffil (6.5 vol%) consisted of drying at 200 °C for 24 h and then heat treating at a higher temperature at the rate of 10 °C/min to the target temperature. However, the Saffil (20 vol%) was directly heated in the target temperature. In this study, the former is called step heat treating, and the latter is direct heat treating. In summary, the Saffil (20 vol%) was treated by direct heat treating and the Saffil (6.5 vol%) by step heat treating. By comparing Tables 7 and 9, one finds that the optimal heat treating temperatures of the Saffil (6.5 vol%)/A06 (1:40) and Saffil (6.5 vol%)/A23 (1:40) were 800 and 1000 °C, respectively, whereas those of the Saffil (20 vol%)/A06 (1:10) and Saffil (20 vol%)/A23 (1:10) were 500 and 200 °C, respectively. All of these preforms have similar binder contents of about 6 or 7 wt%. Thus, the direct heat treat-

ing process lowered the optimal heat treating temperature. This is because the step heat treating process allowed some H_3PO_4 to have sufficient time to escape from the preform with the vapor of water on heating, whereas the direct heat treating process provided no time for this to occur. Therefore, more H_3PO_4 is retained in the Saffil (20 vol%), causing more chemical reaction to form more *in situ* binder. These conditions lead to the occurrence of an earlier over-reaction, thus lowering the optimal heat treating temperature.

4.4.5 Effect of Binder Reactivity on Optimal Heat Treating Temperature

From the last comparison, one finds that the optimal heat treating temperature decreased from 800 to 500 °C for the preform made with phosphate A06 and from 1000 to 200 °C for that with phosphate A23 due to the use of the direct heat treating process. The larger decrease in the optimal heat treating temperature of the preform made with phosphate A23, with a P/Al ratio of 23, compared to that with the phosphate A06, with a P/Al ratio of 6, is probably due to the greater amount of H_3PO_4 entrapped in the preforms on direct heat treating. Therefore, the higher the P/Al ratio of the phosphate, the greater the decrease in optimal heat treating temperature when the process changes from step heat treating to direct heat treating for a similar binder content.

4.5 *Effect of Binder Content on Compressive Strength*

Figure 4 shows that the compressive strength of the Saffil (20 vol%) increases as the binder content increases when the heat treating temperature is 500 °C. It is apparent for all of the phosphate and silica binders. However, Fig. 3 shows a similar result, but it is more complicated due to the effect of heat treating temperatures. If the heat treating temperature is set at a constant, such as 200 °C, it also primarily shows that compressive strength increases as binder content increases. It indicates that the binder content is a relatively important factor contributing to the compressive strength of the preform, but not the only important factor.

The relatively low compressive strength of Saffil (20 vol%)/A03 (1:5)/500 °C compared to its counterparts with phosphates A06 and A23 is probably due to the following. The primary effective binder in this preform is the *ex situ* binder, similar to the preform made with the silica binder, which tends to reach its optimal heat treating temperature at the highest available temperature. Saffil (20 vol%)/A03 (1:10) (see Fig. 5) and Saffil (6.5 vol%)/silica (1:10 or 1:5) (see Fig. 3) all reach their maximum compressive strengths at the highest available temperature. Therefore, it is possible that Saffil (20 vol%)/A03 (1:5) has not yet reached its maximum compressive strength at this temperature.

4.6 *Effect of Binder Reactivity on Compressive Strength*

From Table 7, the maximum compressive strength of Saffil (6.5 vol%)/A06 (1:10) is higher than that of Saffil (6.5 vol%)/A23 (1:10). From Table 8, the maximum compressive strength of Saffil (6.5 vol%)/A06 (1:40) is higher than that of Saffil (6.5 vol%)/A23 (1:40). From Table 9, the maximum compressive strength of Saffil (20 vol%)/A03 (1:10) is the highest, that of Saffil (20 vol%)/A06 (1:10) the second highest, and that of the Saffil (20 vol%)/A23 (1:10) the lowest. Of the three phosphate binders, A03 is the best binder and A06 the second, when considering similar binder content over a full range of temperatures up to 1000 °C. Therefore, in terms of the ratio of P/Al, the lower the ratio of P/Al of the phosphate binder, the higher the maximum compressive strength that can be attained. This could be due to the fact that the *ex situ* binder is more difficult to vaporize than the reaction agent, H_3PO_4, on heating. Hence, the binder that relies more on the *in situ* binder may have more opportunity to lose H_3PO_4 during heating so that it will be unable to reach the same maximum compressive strength as that with more *ex situ* binder.

5. Conclusions

Three phosphate binders, namely phosphate A03, phosphate A06, and phosphate A23, accompanied with the commonly used silica binder, were used to make Saffil fiber preforms for metal-matrix composites. The use of phosphate binders in some conditions leads to a higher compressive strength than the use of silica binder.

The binder content of preforms with the same binder concentration decreases as the heat treating temperature increases. The binder content of a preform increases as the binder concentration increases. When the binder contents of preforms are similar, the heat treating temperatures are dominant.

The major factor influencing the optimal heat treating temperature and the maximum compressive strength is the amount of the reaction medium, the *in situ* binder, in the binder. The more *in situ* binder, the greater the possibility of decreasing the optimal heat treating temperature. Once the amount of *in situ* and *ex situ* binders is well balanced, an optimal heat treating temperature could be determined.

An excessive chemical reaction may not only degrade the compressive strength of the preforms, but may also affect the strength of the resulting MMC. Therefore, the selection of heat treating condition of the preform, binder concentration, and type of binders are very important. When the preform is incorporated into a metal-matrix composite, these variables need to be re-evaluated in terms of the resulting application.

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