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

Part I *Binders*

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Binders are used in preforms from which metal-matrix composites are fabricated by liquid-metal infiltration. This paper (Part I) reports the preparation and characterization of various binders (by themselves). The characterization was in terms of the composition (by atomic absorption spectrometry and X-ray spectrometry), morphology, phases (by X-ray diffraction) and changes upon heating to 1200 °C (by thermogravimetric analysis and mass spectrometry). The binders studied include silica, phosphates (prepared from Al $(OH)_3$ and H_3PO_4) with the P/Al molar ratio ranging from 1–23, sodium silicate and acrylic emulsion. A phosphate binder was in the form of type B aluminium metaphosphate ($Al(PO_3)_3$) at 500 °C when the P/Al atom ratio = 2.2 in the liquid binder, and was in the form of type A aluminium metaphosphate ($Al/(PO_3)_3$) when the atom ratio $\geq$ 5.8 in the liquid binder. Most of the phosphate binders formed type A aluminium metaphosphate ($Al(PO_3)_3$) after heat treatment at 800 °C. The phosphate binder with P/Al atom ratio = 2.2 in the liquid binder formed cristobalite aluminium orthophosphate ($AlPO_4$), and the phosphate binder with P/Al atom ratio = 24 in the liquid binder formed a combination of cristobalite aluminium orthophosphate ($AlPO_4$) and metaphosphate glass after heat treatment at 1200 ° C in argon.

1. Introduction

One of the most economical methods of fabricating metal-matrix composites is liquid-metal infiltration, which may be in the form of squeeze casting, pressure infiltration or variations thereof. In general, liquid-metal infiltration involves infiltrating a liquid metal (or alloy) into a porous preform consisting mainly of the reinforcement, which may be in the form of particles, whiskers or fibres. For whiskers or discontinuous fibres as the reinforcement, the use of a binder in the preform is necessary in order to provide sufficient strength in the preform. Otherwise, the preform may be compressed to a smaller dimension by the pressure encountered during infiltration, thereby making near-net-shape fabrication impossible. Furthermore, the use of a binder enables the preparation of preforms containing a small volume fraction of whiskers or discontinuous fibres which are uniformly distributed. In spite of the importance of binders and preforms [1–3], no prior attention had been given to the relation between preform processing (choice of the binder, heat treatment of the preform, etc.) and the properties of the resulting composites.

Silica colloid is the most widely used binder for preforms used for fabricating metal-matrix composites [4]. This series of three papers reports an acid phosphate binder, which is shown to result in aluminium-matrix composites with superior temperature resistance compared to those made by using the silica binder. Part I of this series is focused on the binder by itself, Part II [5] is focused on the resulting preforms prior to infiltration, while Part III [6] is concerned with the resulting aluminium–matrix composites. Silicon carbide whiskers (SiC_w) and short carbon fibres (C_f) were separately used as reinforcements in this study.

The objectives of this series of papers are as follows:

1. To compare the effectiveness of silica and phosphate binders for fabricating Al/SiC_w and Al/C_f composites;
2. To investigate and understand the effect of the P/Al atom ratio of the acid phosphate binder on the properties of Al/SiC_w;
3. To investigate and understand the effect of the preform heat-treatment conditions on the properties of Al/SiC_w;
4. To understand the nature and effects of the reaction between the phosphate-binder and SiC and that between the phosphate binder and aluminium;
5. To develop Al/SiC_w of improved temperature resistance;

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6. To develop Al/SiC$_w$ of increased tensile strength through the use of acid phosphate binders and annealing of the composites.

2. Status of binder technology

Binders are widely used in ceramic processing. For example, a ceramic was formed by injection moulding with the application of a plastic binder [7]. A binder can be a ceramic or a polymer. Polymer binders, such as polyvinyl alcohol (PVA), are widely used at room temperature because of their ease of application, but they cannot withstand temperatures above about 200 °C. Conventional ceramic binders include oxysulphates, oxychlorides, sodium silicate (also called water glass) and hydraulic cements. In contrast to polymer binders, these ceramic binders have high strength at room temperature, but they start to disintegrate at 200–300 °C and may give unsatisfactorily low strength at 500–800 °C. Water glass tends to melt at about 900 °C, probably due to decomposition, resulting in low strength at high temperatures [7]. The binders mentioned above are not suitable for making preforms in this work, because, before the metal infiltration, the preform is required to be heated up to 700–800 °C. Binders having high-temperature resistance, such as those binders normally used for refractories, are suitable for this work.

A study of the properties of SiC-bearing materials used in recuperators shows that the silicon carbide materials were produced using a nitride binder [8]. Another study showed that refractory specimens were made with fused alumina, tabular alumina and fused mullite as grog (coarse oxide particle) materials and ground calcined alumina (used alone, with phosphoric acid or ground silica sand) as a binder [9]. Karasik *et al.* [10] reported a study on the production of corundum–SiC-bearing concrete parts using a liquid-glass binder. Hot-pressed SiC with the addition of 2 wt % BeO as binder was studied for its electrical properties after irradiation with electrons and neutrons [11]. The last example is a preparation of pressureless-sintered SiC [12], where the sintering additives were prepared from aluminium hydroxide and yttrium hydroxide. These additives were soluble in water and resulted in a binder. A β-SiC powder was mixed with the additive solution and sintered at 2150 °C without pressure. The oxides formed from the additive promoted sintering. Aluminium, silicon and yttrium oxides were precipitated in the sintered body. Table I shows the applications of various binders for binding ceramic materials.

A widely used binder in the field of refractory is the phosphate binder. There are numerous kinds of phosphate binder. A study of the mechanical properties of an unsintered SiC compact bonded by $AlPO_4$ glass has been reported [13]. Pirogov *et al.* [14] studied the optimum content of graphite and SiC additives in a mullite–corundum body produced using a binder based on orthophosphoric acid (H_3PO_4). The reactivities of several calcined aluminas with orthophosphoric acid at fairly low curing temperatures were studied by Toy and Whittemore [15], who showed that the compressive strength was inversely proportional to the surface area of the calcined alumina used in the bond, due to the formation of the crystalline $AlPO_4$ phase from the calcined alumina. A glassy phase and possibly an aluminium metaphosphate ($Al(PO_3)_3$) phase are effective bonding phases. Gitzen *et al.* [16] have developed refractory castables composed of a sintered aluminium oxide grog bonded with phosphoric acid (H_3PO_4). These castables are characterized by high bond strength and remarkable resistance to erosion over a wide temperature range. Monoaluminium phosphate ($Al\,(H_2PO_4)_3$) and magnesium phosphate ($Mg(H_2PO_4)_2$), commercially available from Albright and Wilson Americas, were reported to be suitable for the applications for steel coating, refractories and foamed ceramics [17].

TABLE I Applications of various binders for binding ceramics

Binders	Materials bound
Organic polymer	
Polyvinyl alcohol	Ceramics (SiC, Si_3N_4)
Polyvinyl butyral	Metal to ceramic (particles)
Polyethylene	Glass powder
Acrylic resins	
Wax emulsion	
Polyethylene glycol	
Organosilicon polymer	
Alcohol + wax	
Thermoplastic resin + N_2	
Silicate binders	
Alkali metal silicate	Ceramic (SiC)
Water glass (sodium silicate)	Corundum–SiC
Aluminosilicate	Coating
	General use
Silica binders	
Silica	Ceramic (SiC)
Silica + latex	Aluminosilicate fibres
	Alumina fibres
Nitride binder	
Silicon nitride	SiC
Oxide binder	
BeO	SiC
Phosphate binders	
H_3PO_4	Alumina
$Al_2O_3 + H_3PO_4$	Aluminium silicate
$AlPO_4$	Mg–Al silicate
$AlPO_4 + (NH_4)_3PO_4 + Na_3PO_4$	Zr silicate
$H_3PO_4 + C + SiC$	ZrO_2
	SiC
	Mullite-corundum
Hydroxide binders	
$Al(OH)_3 + Y(OH)_3 + H_2O$	SiC
Other binders	
Oxysulphates	General use
Oxychlorides	
Hydraulic cements	

There are three methods of utilizing phosphate bonding in refractories [16]: (1) the use of siliceous materials with phosphoric acid; (2) the use of oxides with phosphoric acid; and (3) the direct addition or formation of an acid phosphate. The acid phosphate in Method 3 is prepared by the addition of an acid (e.g. phosphoric acid) to a phosphate solution. The phosphoric acid itself acts as a bonding material. Generally, additions of aluminium, magnesium, iron and beryllium greatly increase its bonding power [18];

these cations are all amphoteric or weakly basic and have moderately small atomic radii. In contrast, additions of calcium, barium and thorium decrease the bonding power; all these cations are either highly basic or have large atomic radii [18]. The optimum bonding is obtained only with weakly basic or amphoteric cations having moderately small atomic radii [18]. 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.

Because the addition of aluminium increases the bonding power, aluminium phosphates were widely used as binders for ceramics and were adopted in this study. In this work, the aluminium phosphate binders were used at various values of P/Al atom ratio. All the aluminium phosphate binders contain phosphoric acid in excess of what is needed to form aluminium phosphates. Therefore, they can be called acid phosphates. When an acid phosphate is used to bond SiC whiskers (a siliceous material), the situation corresponds to the combination of Methods 1 and 3. When an acid phosphate is used to bind carbon fibres (not siliceous material), Method 3 is the case. In particular, PO_4^{3-}, $P_2O_7^{4-}$ and PO_3^- are called orthophosphate, pyrophosphate and metaphosphate, respectively.

The Al_2O_3–P_2O_5–H_2O system has been the subject of many studies [18–24]. The chemistry of aluminium phosphates is based on compounds with P/Al atom ratios of 1/1 ($AlPO_4 \cdot xH_2O$) and 3/1 ($Al(H_2PO_4)_3$). The monoaluminium phosphate ($Al(H_2PO_4)_3$) transforms to aluminium triphosphate ($AlH_2P_3O_{10}$) via dehydration upon heating at 230 °C. After that, further heating causes the formation of type B aluminium metaphosphate ($Al(PO_3)_3$ (B)) via dehydration at about 500 °C. Type B aluminium metaphosphate transforms to type A aluminium metaphosphate upon heating above 800 °C. Further heating to about 1200 °C causes the formation of metaphosphate glass. If it is further heated above 1200 °C, decomposition occurs and the cristobalite $AlPO_4$ forms, together with the release of phosphoric oxide (P_2O_5). Different transformations at different temperatures apply to other P/Al atom ratios.

The low-temperature form, type B aluminium metaphosphate ($Al(PO_3)_3$(B)), has a chain structure in which the PO_4 tetrahedra are linked together to form infinite $(PO_3^-)_n$ chains; the high-temperature form, type A aluminium metaphosphate ($Al(PO_3)_3$ (A)), has a ring structure [24, 25]. The cristobalite aluminium orthophosphate ($AlPO_4$) has a similar crystal structure to cristobalite silica (SiO_2), as Al + P in $AlPO_4$ is equivalent to Si_2 in Si_2O_4. In addition, aluminium orthophosphate ($AlPO_4$) exists as quartz (berlinite) and tridymite.

3. Binder preparation

In this work, two types of binder were used to prepare α-SiC whisker preforms. The first type was silica, which was used at a concentration of 1 part of silica colloid (30 wt % silica in water, Fisher Scientific Co.) in 6 parts of water. The other type was phosphates. Five different phosphate solutions were used in this study. Four of them were made in our laboratory and the fifth one, called mono-aluminium phosphate (MAP, ($Al(H_2PO_4)_3$) solution, was obtained from Albright and Wilson Americas. The phosphate solutions were prepared by mixing 1 part of aluminium hydroxide ($Al(OH)_3$, J. T. Baker Chemical Co.) with various parts of phosphoric acid (H_3PO_4, 85% Technical Grade, Riverside Chemical Co.), so that these solutions have the calculated atom ratio P/Al [19–21, 24] of 1, 3, 6, 12 and 23. For convenience, the corresponding phosphate binders were denoted A01, A03, A06, A12, and A23, respectively. After mixing the aluminium 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 the solids were dissolved. The solution with the atom ratio P/Al of 1 could not be made because the fast chemical reaction resulted in the formation of a solid compound. The atom ratio P/Al for the mono-aluminium phosphate ($Al(H_2PO_4)_3$) solution, denoted MAP, was 3 from the data sheet supplied by the manufacturer. All phosphate binders (except the phosphate MAP binder) were made at a concentration of 1 part of a phosphate solution in 15 parts of water, unless stated otherwise. The phosphate MAP binder was made at a concentration of 1 part of the phosphate MAP solution in 8.6 parts of water. Using this ratio was due to the presence of 0.4 part of water in the as-received phosphate MAP solution, so that the real binder/water ratio was also 1/15. The above silica or phosphate concentrations were chosen in order to obtain preforms containing around 3–5 wt % silica or phosphate. The amount of silica or phosphate in the preforms increased with decreasing water content in the slurry.

Four binders, namely silica, phosphate, water glass and acrylic emulsion, were chosen to investigate their binding ability with chopped carbon fibres. They were prepared in an aqueous solution. The silica binder was prepared with 1 part of silica colloid (30 wt % silica in water, Fisher Scientific Co.) in 6 parts of water. The phosphate binder was used at a concentration of 1 part of phosphate A23 solution in 15 parts of water. The water glass binder was used at a concentration of 1 part of water glass (sodium silicate, from Rutland Fire Clay Co.) in 6 parts of water. The acrylic emulsion binder was used at a concentration of one part of acrylic emulsion (50% acrylic polymer in water, Latex, Dow Chemical Company) in 6 parts of water.

The silica binder is a colloid, which has a dispersion of fine particles in water. The acrylic emulsion binder is a colloid of two liquids. The water is driven off by evaporation when heated, leaving the binder particles behind to interlock the fibres together. The phosphate and water glass binders act like glues. Each is initially in a liquid form, but after heating it precipitates to form a solid.

Drying treatment of the binder was carried out by heating the binder at 200 °C (except for the acrylic emulsion binder) for at least 1 week. After the 1 week heat treatment at 200 °C, most binders were dried completely. However, the phosphate A06, A12 and

A23 binders were still not totally dried. The phosphate A23 binder was especially like an emulsion with a high viscosity. The acrylic emulsion binder was dried at 100 °C.

The silica binder was heat treated in air at 4 different temperatures, 500, 800 and 1100 °C, after the drying treatment. The phosphate binders were heat treated in air at 500, 800 and 1100 °C or in argon at 1200 °C after the drying treatment. The water glass binders were heat treated in air at 1100 °C after the drying treatment at 200 °C.

The temperature was increased from room temperature at the rate of 10 °C min^{-1}, kept at the target temperature (500, 800, 1100 or 1200 °C) for 4 h, and then cooled to room temperature at an initial rate of 10 °C min^{-1} and finally (below around 650 °C) at the rate corresponding to furnace cooling (i.e. cooling rate $\leq$ 10 °C min^{-1}).

4. Binder characterization

The binders were characterized without SiC whiskers or carbon fibres to obtain information as a reference.

Atomic absorption analysis of the diluted phosphate binders A03, A06, A12 and A23 and phosphoric acid was performed by using a Perkin–Elmer 560 Atomic Absorption Spectrophotometer with an HGA-2200 Graphite Furnace. Table II shows the contents of aluminium and phosphorus in the diluted phosphate solutions and the phosphoric acid. The resulting P/Al atom ratios were comparable to the expected ratios of 3, 6, 12 and 23. The presence of aluminium in phosphoric acid was due to the impurity in the acid.

Fig. 1 shows scanning electron micrographs of the silica binder after heating at 200, 800 and 1100 °C (in air). The silica binder heated at 500 °C is not shown in Fig. 1 because it is similar to that of 200 °C. The silica

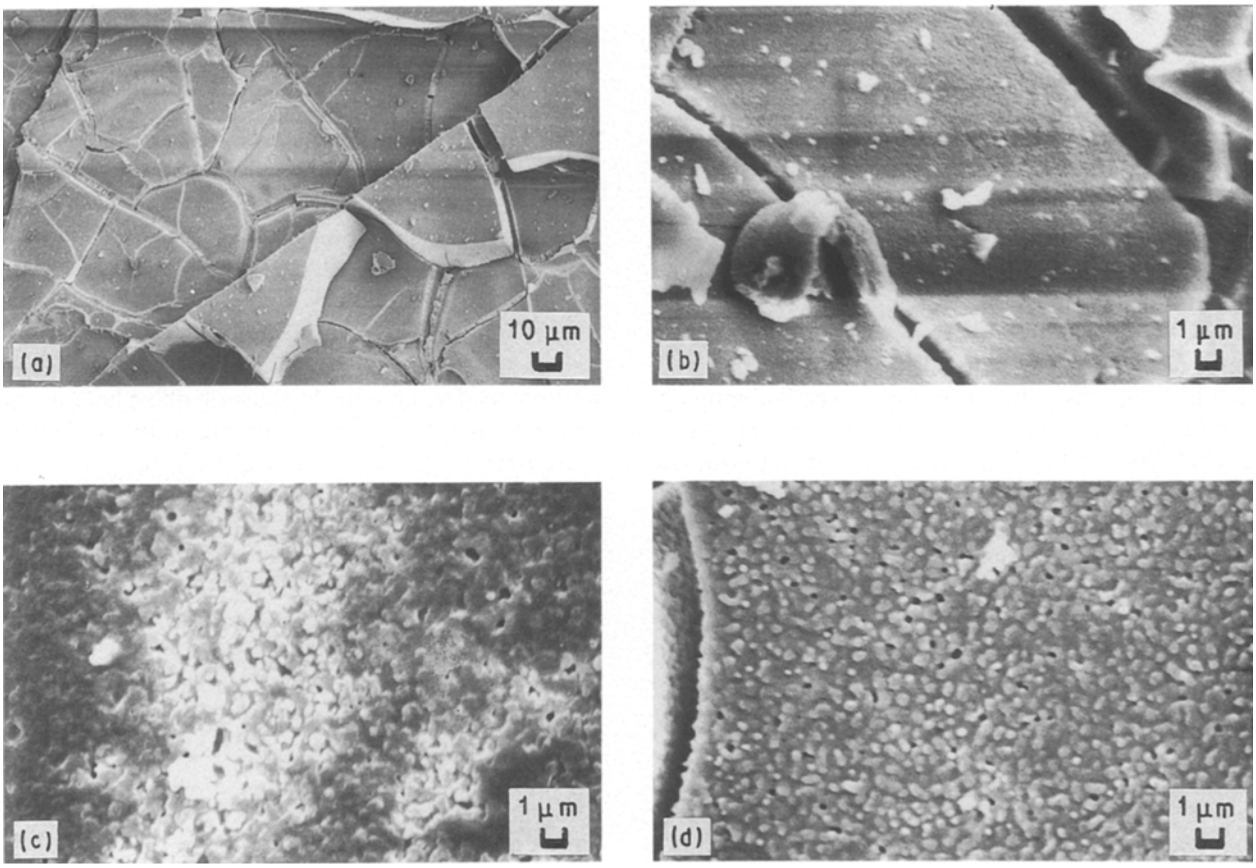

Figure 1 Scanning electron micrographs of the silica after heat treatments at (a, b) 200, (c) 800 and (d) 1100 °C (in air).

TABLE II Contents of aluminium and phosphorus in the liquid binders

Binder	Al (p.p.m) (by weight)	P (p.p.m) (by weight)	P/Al (by weight)	P/Al (by atom)
A03	101.8 (4.9)[a]	255 (15)	2.5	2.2
A06	61.6 (5.4)	411 (17)	6.7	5.8
A12	30.9 (3.1)	329 (9)	11	9.3
A23	24.5 (3.0)	660 (24)	27	24
Phosphoric acid	0.2 (0.1)	760 (23)	3800	3300

[a] Values in parentheses shows the standard deviation.

binder showed cracks after heating at 200 or 500 °C, but showed a grainy microstructure after heating at 800 or 1100 °C. The grain was smaller when the heat-treatment temperature was higher (at 1100 °C). Fig. 2 shows the X-ray diffraction XRD patterns (obtained with CuK_α radiation, as for all XRD patterns in this paper) of the silica binder after heat treatment in air at 200, 500, 800 and 1100 °C. The silica was amorphous after heating at 200 and 500 °C; as shown by XRD. The silica started to form cristobalite SiO_2 after heating at 800 °C and transformed to form a mixture of cristobalite and tridymite SiO_2 1100 °C, as shown by XRD. The crystallization was accompanied by the appearance of a grainy microstructure.

The phosphate A01 binder after heat treatment at 500 and 800 °C locally showed a smooth morphology and globally high porosity after heat treatment at both temperatures. Fig. 3 shows the XRD patterns of the phosphate A01 binder after the same heat treatment. The phosphate A01 binder formed mainly the berlinite aluminium orthophosphate ($AlPO_4$), together with some type B aluminium metaphosphate ($Al(PO_3)_3$) at 500 °C. At 800 °C, the aluminium metaphosphate transformed from type B to type A. Therefore, the resulting phase of the phosphate A01 binder became mainly berlinite aluminium orthophosphate ($AlPO_4$), together with some type A aluminium metaphosphate ($Al(PO_3)_3$).

Fig. 4 shows the XRD patterns of the phosphate A03 binder after heat treatment at 200, 500, 800, 1200 °C (in air) and 1200 °C (in argon). The phosphate binder A03 after heat treatment at 200 °C was in the form of the type C aluminium hydrogen phosphate (Al $(H_2PO_4)_3$). At 500 °C, it changed to type B aluminium metaphosphate ($Al(PO_3)_3$). It locally showed a quite smooth morphology and globally showed very low porosity at this temperature. At 800 °C, the type A aluminium metaphosphate ($Al(PO_3)_3$) emerged and became the second phase. The binder locally showed a flake or needle-like morphology and globally showed low porosity. When the phosphate A03 binder was heat treated at 1200 °C in air, the cristobalite aluminium orthophosphate ($AlPO_4$) became the dominant phase, accompanied by a minor amount of type A aluminium metaphosphate ($Al(PO_3)_3$). The morphology of the binder after this heat treatment locally showed a grainy structure and globally showed medium porosity. On the other hand, when the phosphate A03 binder was heat treated at 1200 °C in argon rather than air, a single phase of cristobalite aluminium orthophosphate ($AlPO_4$) was formed. The formation of cristobalite $AlPO_4$ is mainly due to the dissociation of type A $Al(PO_3)_3$ [23, 26]. After this heat treatment, the binder morphology locally showed finer, but still smooth, grainy structure and globally showed high porosity. The porosity change from 800–1200 °C in air or in argon was probably due to the release of P_2O_5 when the dissociation of type A aluminium metaphosphate $(Al(PO_3)_3$ occurred. That the locally grainy structure for the binder after heating

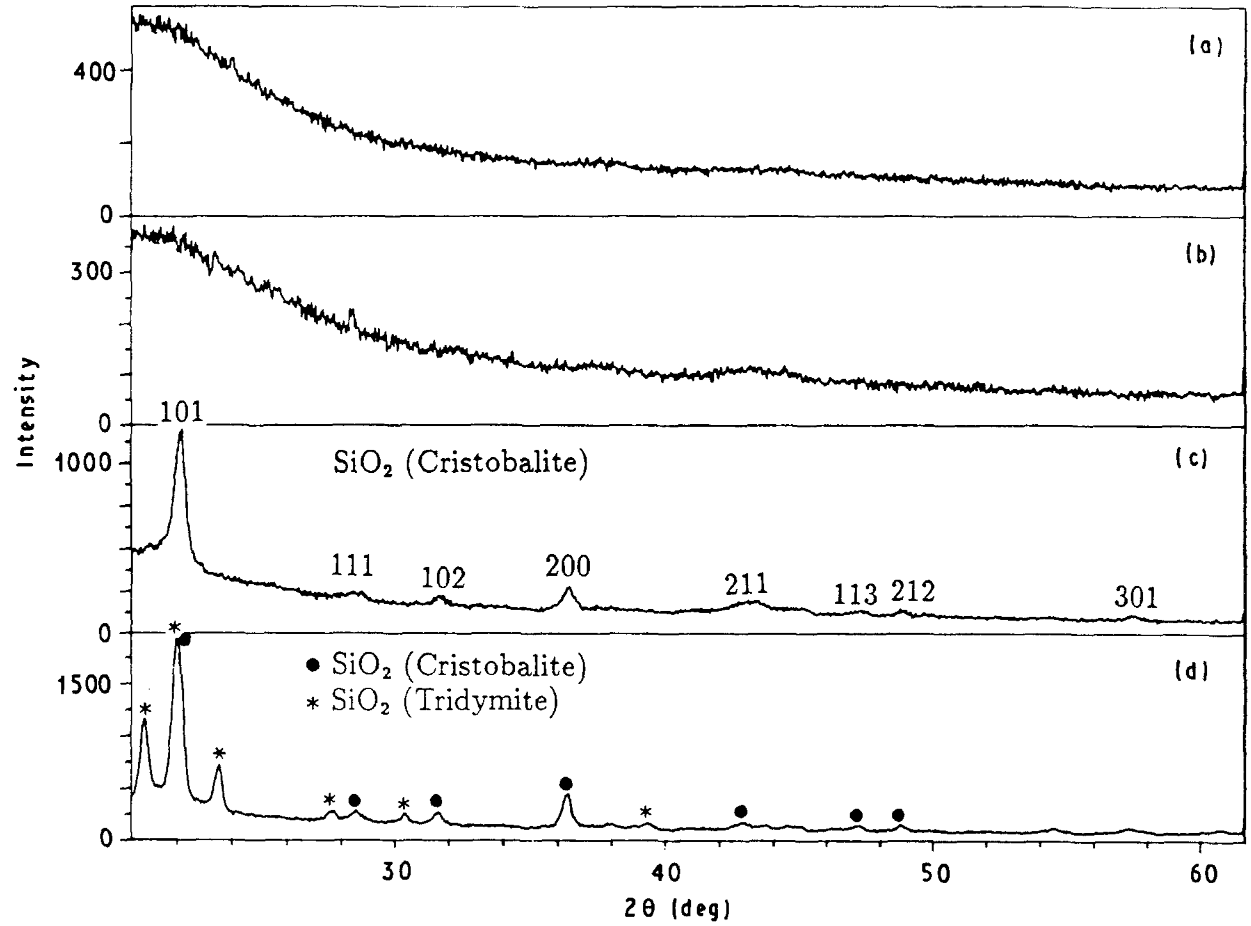

Figure 2 XRD patterns of the silica after heat treatments at (a) 200, (b) 500, (c) 800 and (d) 1100 °C (in air).

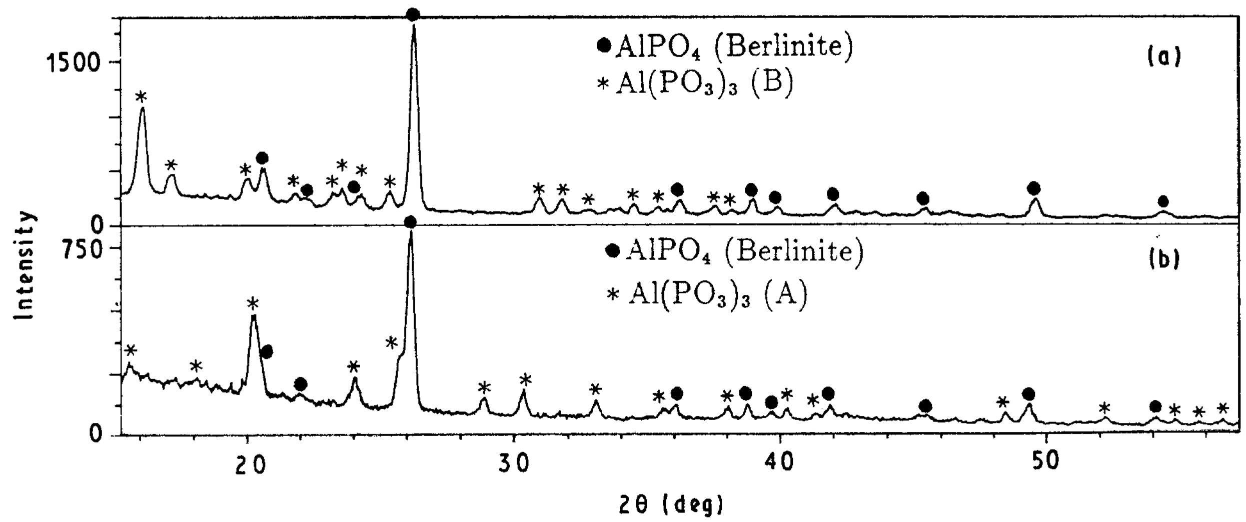

Figure 3 XRD patterns of the phosphate A01 after heat treatments at (a) 500 and (b) 800 °C.

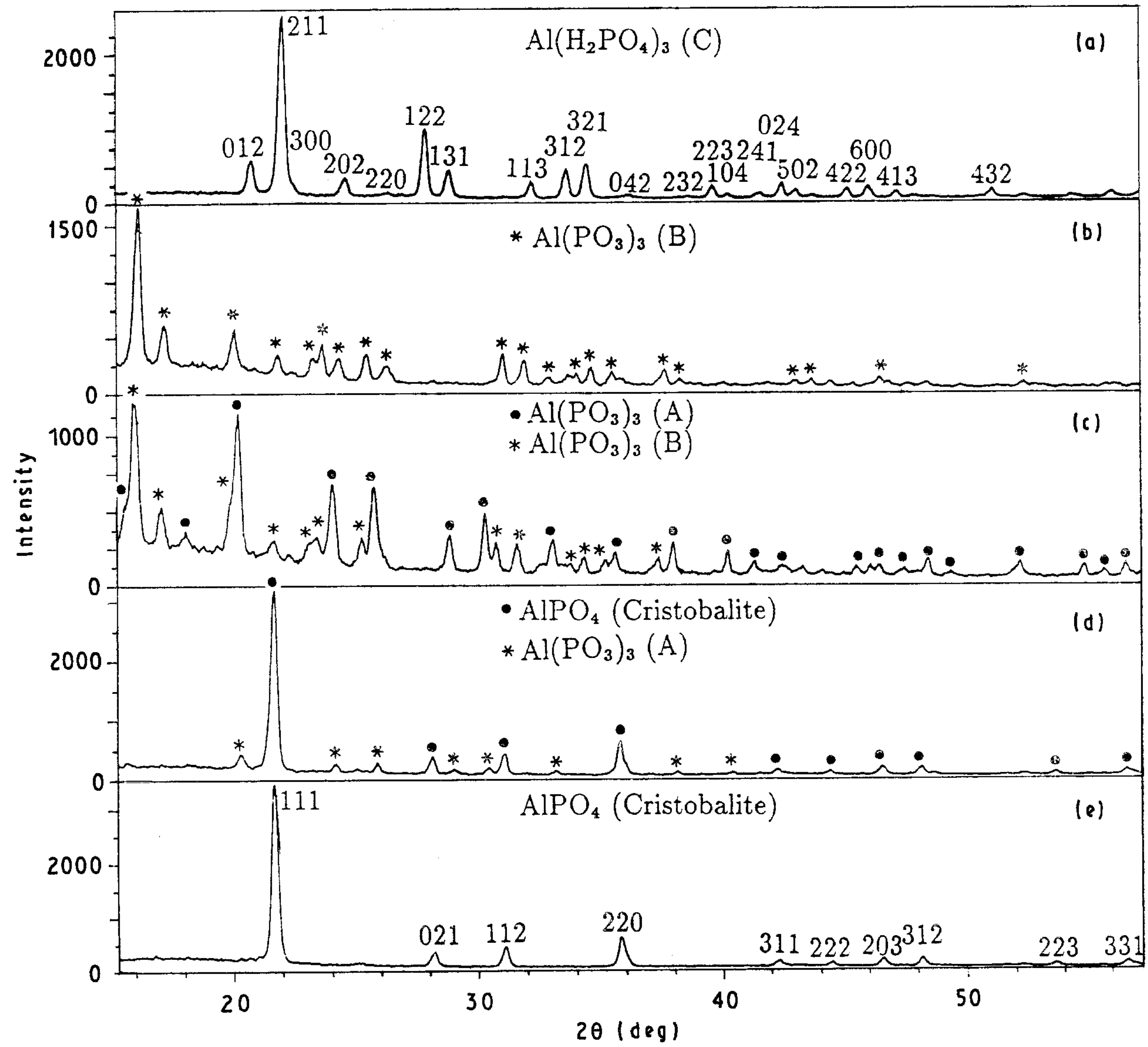

Figure 4 XRD patterns of the phosphate A03 after heat treatments at (a) 200, (b) 500, (c) 800, (d) 1200 °C (in air) and (e) 1200 °C (in argon).

in argon was finer than that in air was probably due to the more severe release of P_2O_5 from the dissociation of all the type A aluminium metaphosphate ($Al(PO_3)_3$ in argon, as the oxygen partial pressure in air may inhibit the P_2O_5 release.

The phosphate A06 binder locally showed smooth morphology at 500 °C and less smooth morphology at 800 °C; both were globally medium in porosity. The phosphate A12 binder locally showed a rougher morphology at 500 °C, compared to that of the phosphate

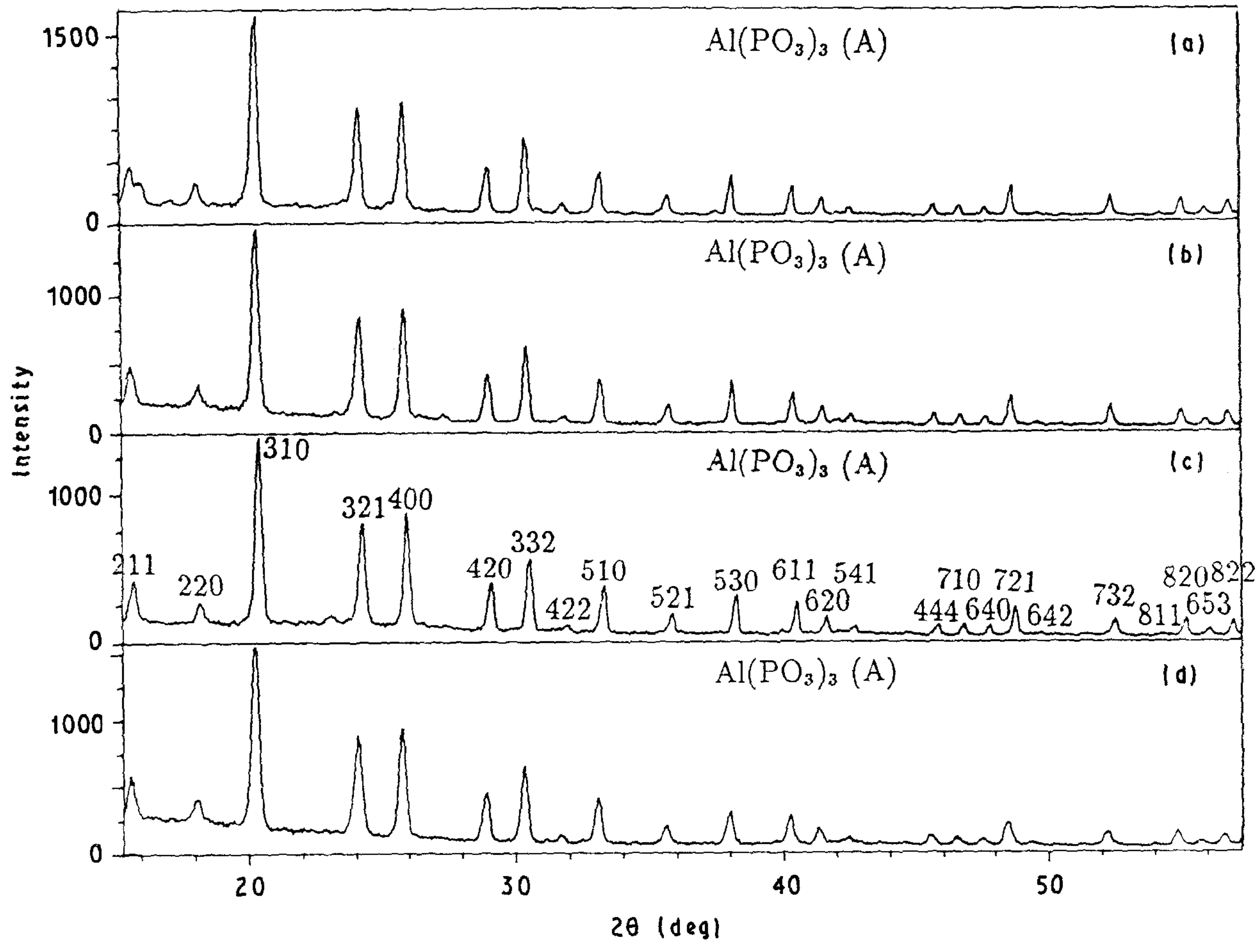

Figure 5 XRD patterns of the phosphate A06 after heat treatments at (a) 500 °C and (b) 800 °C, and those of the phosphate A12 at (c) 500 °C and (d) 800 °C.

binder A06; at 800 °C, it showed a less rough morphology (with small holes), compared to the A12 binder at 500 °C; the A12 binder globally showed medium porosity at both temperatures. The formation of small holes for the phosphate A12 binder at 800 °C was probably due to the release of the phosphorus in a certain form, which resulted from the crystallization of type A aluminium metaphosphate. Fig. 5 shows the XRD patterns of the phosphate binders A06 and A12 after heat treatment at 500 and 800 °C. After heat treatments at 500 and 800 °C, both phosphate binders A06 and A12 formed type A aluminium metaphosphate ($Al(PO_3)_3$).

Fig. 6 shows scanning electron micrographs of the phosphate A23 binder after heat treatment at 500, 800 and 1100 °C (in air). No micrograph corresponding to 200 °C is shown because this sample could not be viewed under SEM. The reason is that the sample heated at 200 °C remained wet, like syrup, even after a week of drying at this temperature. Fig. 7 shows the XRD patterns of the phosphate A23 binder after heat treatment at 200, 500, 800, 1100 °C (in air) and 1200 °C (in argon). The phosphate A23 binder remained amorphous after heating at 200 °C, as shown by XRD, but crystallization occurred after heating at 500 or 800 °C to form mainly type A aluminium metaphosphate ($Al(PO_3)_3$). The morphology of this binder was locally rough with high porosity globally after heat treatment at 500 and 800 °C. After heating at 1100 °C in air, the phosphate A23 binder became amorphous again. This phase should be the metaphosphate glass, which had been previously reported [23, 26]. The morphology of this binder at 1100 °C in air was locally smooth but globally high in porosity (Fig. 6). After heating at 1200 °C in argon, the phosphate A23 binder was mainly amorphous, although it was accompanied by a minor amount of a crystalline phase, which was probably the cristobalite aluminium orthophosphate ($AlPO_4$). The morphology was very smooth locally, with low porosity globally. That the phosphate A23 binder after heat treatment at 1100 °C in air and 1200 °C in argon both locally showed smooth morphology was related to the fact that the dominant phase for both cases was amorphous.

Fig. 8 shows the XRD patterns of the phosphate MAP after heat treatment at 200, 500, 800, 1200 °C (in air) and 1200 °C (in argon). The phosphate MAP binder formed mainly aluminium hydrogen phosphate ($AlH_2P_3O_{10}$) after heat treatment at 200 °C. Similar to the case of the phosphate A03 binder, the phosphate MAP binder, after heating at 500 °C, formed the type B aluminium metaphosphate ($Al(PO_3)_3$). The morphology locally also showed a smooth appearance but globally showed high porosity. After heating at 800 °C, the phosphate MAP binder had a part of the aluminium metaphosphate ($Al(PO_3)_3$) transformed from type B to type A. The morphology locally also showed a flake- or needle-like structure, which was

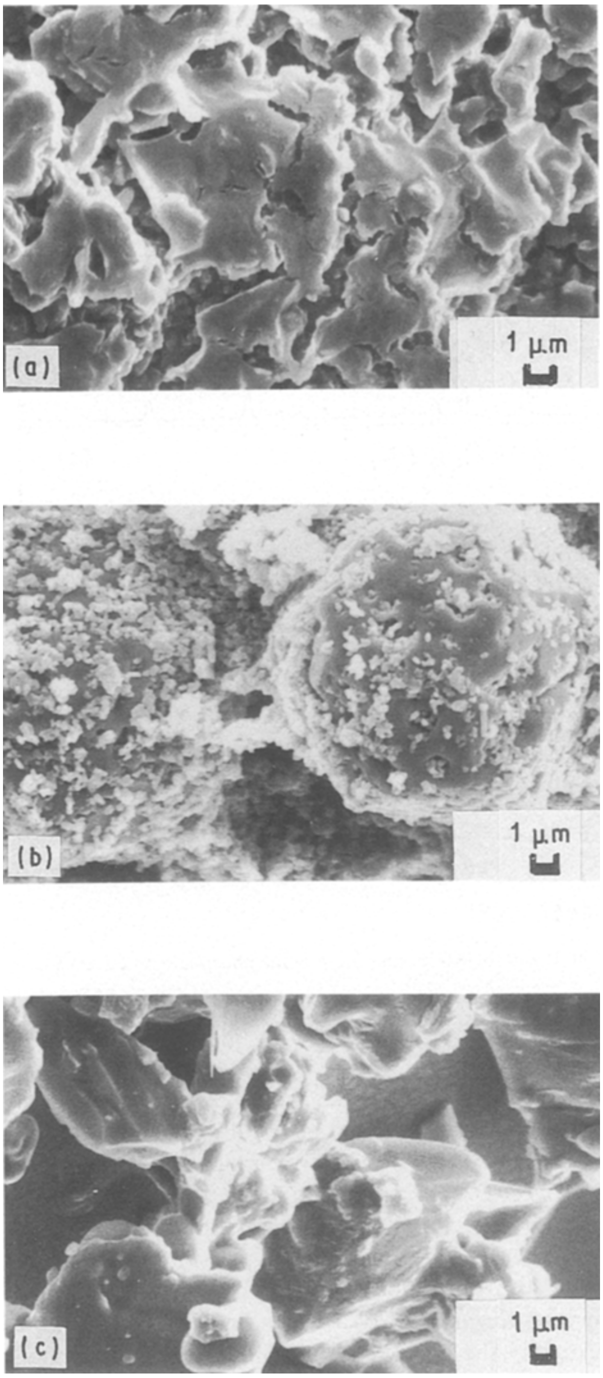

Figure 6 Scanning electron micrographs of the phosphate A23 binder after heat treatments at (a) 500, (b) 800 and (c) 1100 °C (in air).

TABLE III P/Al atom ratio of the phosphates after heat treatments

Binder	500 °C	800 °C	Released H_3PO_4[a] (wt %)
A01	1.97	1.94	–
A03	3.50	3.32	5
A06	3.81	3.40	12
A12	4.22	3.63	15
A23	4.80	3.95	19

[a] H_3PO_4 and/or other forms of phosphorus.

similar to that of the phosphate A03 binder at the same temperature with the same crystalline phase, but globally showed high porosity. After heating at 1200 °C in air, the phosphate MAP binder became a mixture of cristobalite aluminium orthophosphate ($AlPO_4$) and type A aluminium metaphosphate ($Al(PO_3)_3$). The morphology locally showed a smooth appearance and globally showed low porosity. On the other hand, the phosphate MAP binder was in the form of cristobalite aluminium orthophosphate ($AlPO_4$) alone when heated at 1200 °C in argon. The morphology became locally smooth and grainy and globally high in porosity. The high porosity was again probably due to the release of P_2O_5 resulted from the dissociation of type A aluminium metaphosphate ($Al(PO_3)_3$) [23, 26].

The energy-dispersive X-ray spectrometry (EDS) system in Hitachi SEM S800 was used to analyse the P/Al ratio in the phosphates A01, A03, A06 and A23 after heating at either 500 or 800 °C. In order to avoid the extraneous signals due to the aluminium sample holder, the sample was secured by using carbon paste on a 3 mm thick dense graphite plate, which was placed on the sample holder. Table III shows the measured values of the P/Al atom ratio of these phosphate binders after heating at 500 and 800 °C. The measured values are much lower than the calculated values of 6 and 23 for the phosphate binders A06 and A23, but are higher than the calculated values of 1 and 3 for the phosphate binders A01 and A03 after heating at 500 or 800 °C. This may be because the aluminium hydroxide ($Al(OH)_3$) did not totally dissolve in the phosphoric acid during the course of binder preparation for the phosphates A01 and A03 binders due to the low phosphoric acid concentrations in these binders. The change of the heating temperature from 500 °C to 800 °C caused the P/Al ratio to decrease due to the release of phosphoric acid. The fractional weight loss due to phosphoric acid (or other forms of phosphorus) release increased with increasing P/Al ratio in the original binder.

Thermogravimetric analysis (TGA) was performed to analyse the weight change of the phosphate binders upon temperature scanning. Fig. 9 shows the TGA curve of the phosphate A03 binder from 200–1300 °C at a heating rate of 50 °C min^{-1} in a nitrogen atmosphere. The phosphate binder A03 was dried at 200 °C before the TGA measurement, which was performed using a Perkin–Elmer Series 7 thermal analysis system. The result shows that the weight decreased by about 15% when the temperature increased from 200 °C to 600 °C. The weight decrease of the phosphate A03 binder could be due to two different phase transitions. The first one occurred from about 200–400 °C and the second one occurred from about 400–620 °C. These two phase transitions could mainly correspond to the transformation from type C aluminium hydrogen phosphate ($Al(H_2PO_4)_3$) through aluminium hydrogen phosphate ($AlH_2P_3O_{10}\cdot(2\text{–}3)H_2O$ [27] to type B aluminium metaphosphate ($Al(PO_3)_3$), together with the release of other species, such as water or phosphorus in a certain form. The third weight change, about 2 wt %, occurred from about

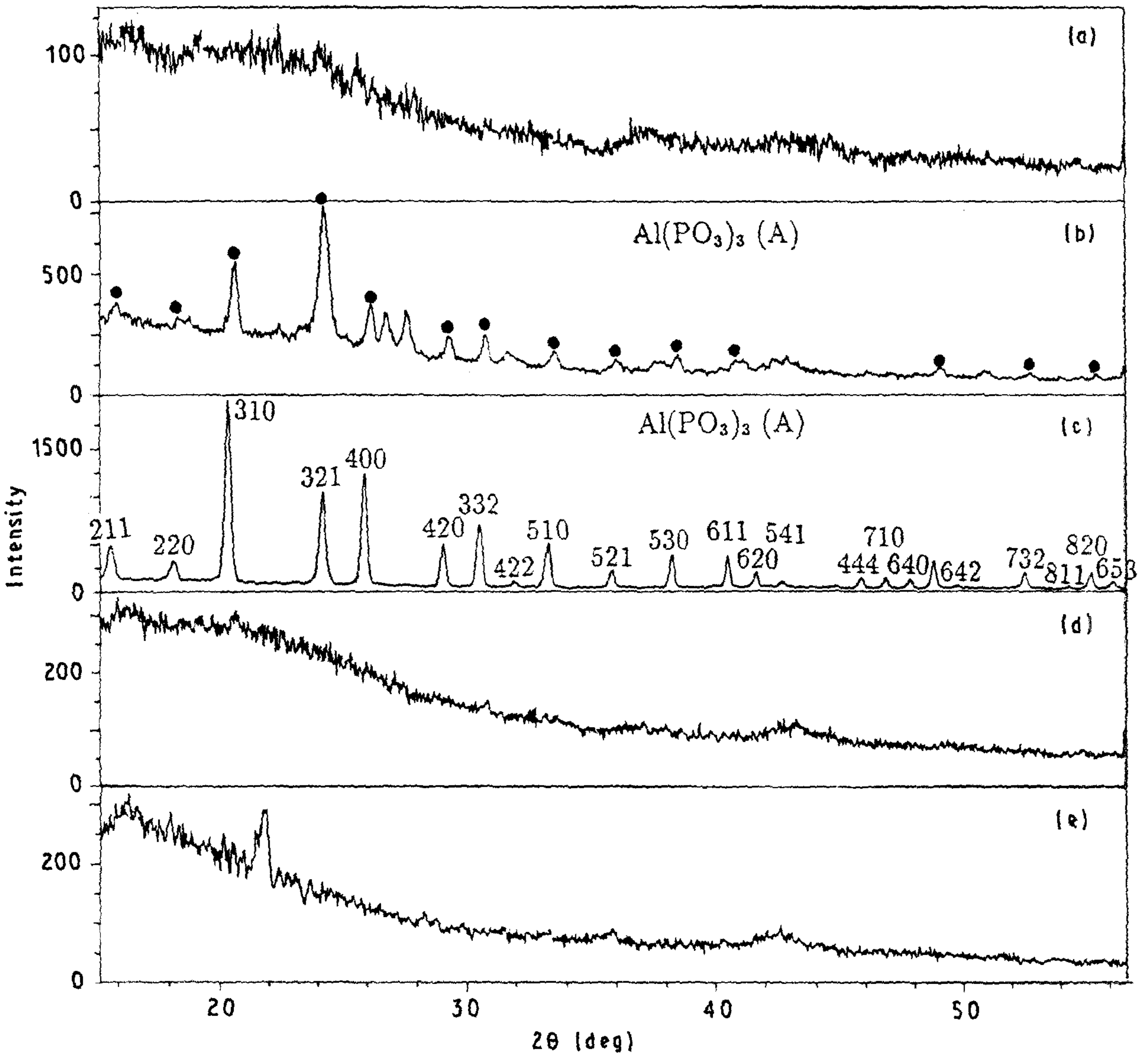

Figure 7 XRD patterns of the phosphate A23 binder after heat treatments at (a) 200, (b) 500, (c) 800, (d) 1100 °C (in air) and (e) 1200 °C (in argon).

620–940 °C. It could correspond to the release of phosphorus in a certain form.

The last weight change shown in Fig. 9 started at about 1000 °C and extended to the end of the temperature scan. The weight decrease was believed to be larger than 17 wt % because the phase transition was not totally complete at the end of the run. Corresponding to this weight decrease could be the dissociation of type A aluminium metaphosphate ($Al(PO_3)_3$), which resulted in the formation of cristobalite aluminium orthophosphate ($AlPO_4$), as shown in Fig. 4d, possibly accompanied by the release of phosphorus oxide (P_2O_5).

Theoretically, the weight loss (based on the original weight of $Al(H_2PO_4)_3$) should be 17% for the dehydration from $Al(H_2PO_4)_3$ (C) to $Al(PO_3)_3$ (B) (200–500 °C) with the release of H_2O, 0% for the transformation from $Al(PO_3)_3$ (B) to $Al(PO_3)_3$ (A) (500–800 °C) and 45% for the dissociation from $Al(PO_3)_3$ (A) to cristobalite $AlPO_4$ with the release of P_2O_5 (800–1300 °C). Comparison of the theoretical weight loss (17%) due to the combination of the dehydration (17%) from $Al(H_2PO_4)_3$ to type B $Al(PO_3)_3$ and the transformation (0%) from type B to type A $Al(PO_3)_3$ with the TGA value of 15% and 2%, respectively, indicates that the weight loss of the binder was totally due to the dehydration of $Al(H_2PO_4)_3$. The theoretical weight loss of 45% due to the dissociation from type A $Al(PO_3)_3$ to cristobalite $AlPO_4$, was larger than the observed value of 17%, because the transition was not yet complete at the end of the TGA scan.

Fig. 10 shows the TGA result of the phosphate A23 binder after the 500 °C heat treatment, as obtained by operating the DuPont 951, thermogravimetric analyser from 35–800 °C at a heating rate of 20 °C min^{-1} in a nitrogen purge (50 cm^3 min^{-1}). The result shows no significant weight change step below 500 °C. A large weight decrease, about 40 wt %, was observed from 500–800 °C. The phosphate A23 binder formed mainly type A aluminium metaphosphate ($Al(PO_3)_3$) at 500 °C and showed complete crystallization at 800 °C, as shown in Fig. 7. However, the large weight decrease cannot be due to the occurrence of the crystallization of type A aluminium metaphosphate ($Al(PO_3)_3$). A possible reason for the large weight

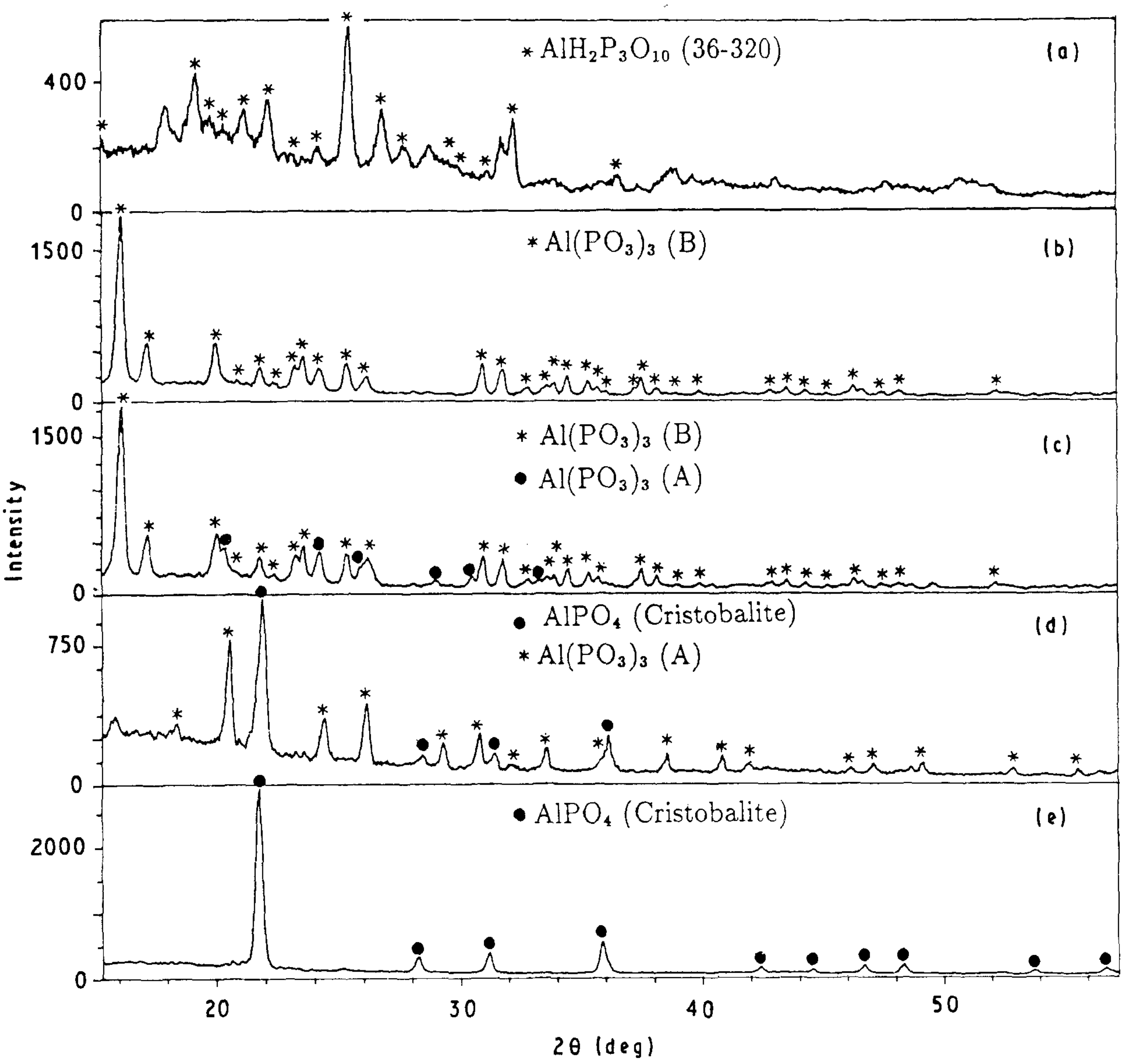

Figure 8 X-ray diffraction patterns of the phosphate MAP after heat treatments at (a) 200, (b) 500, (c) 800, (d) 1200 °C (in air) and (e) 1200 °C (in argon).

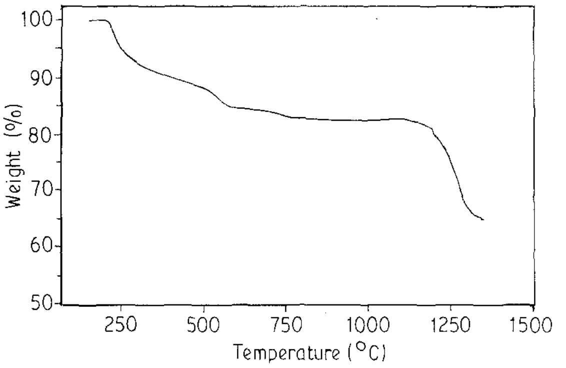

Figure 9 TGA curve of the phosphate A03 binder after drying at 200 °C.

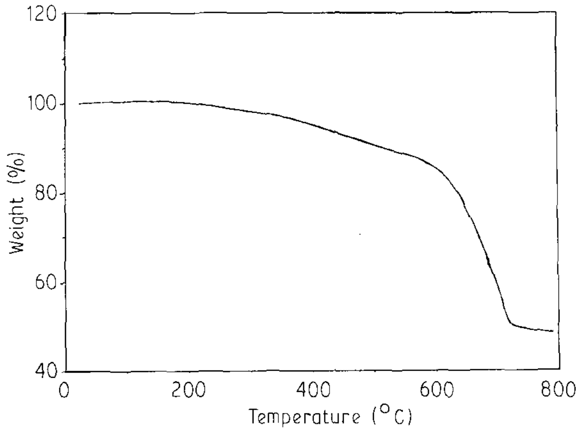

Figure 10 TGA curve of the phosphate A23 binder after heat treatment at 500 °C.

decrease was attributed to the release of the extra phosphorus in a certain form. Such a gas release was therefore investigated by mass spectrometry.

A VG Instruments, Inc., SX300 quadrupole mass spectrometer was operated from 500–800 °C at a heating rate of 20 °C min^{-1}. The mass spectrometer was scanned continuously at 1 AMU s^{-1} from 1–150 AMU. Table IV shows the average partial pressures of species observed in the scanned mass range for the phosphate A03 and A23 binders after heat treatment at 500 °C. Nitrogen and a part of the oxygen were from the air, but hydrogen, oxygen and a small amount of phosphorus were released for the case of the phosphate A03 binder. This is reasonable because of two possibilities: firstly, there may be still some residue of type C aluminium hydrogen phosphate ($Al(H_2PO_4)_3$) remaining in the binder after the heat treatment at 500 °C; secondly, a small amount of the excess phosphoric acid in the binder may release the phosphorus in a certain form. For the case of the phosphate A23 binder, in addition to more hydrogen, oxygen and phosphorus, minor amounts of phosphorus oxides were evolved. This indicates that the release of extra phosphorus was indeed true for this binder in this temperature range. The presence of hydrogen, phosphorus and various kinds of phosphorus oxides (PO, PO_2, PO_3 and PO_4) in the mass spectrum shows that the release of the extra phosphorus can be in the form of phosphorus or phosphorus oxide. The amount of released extra phosphorus was larger for the phosphate A23 binder than for the phosphate A03 binder. The release of phosphorus in the form of phosphoric acid (H_3PO_4) was possible, though peaks at 1 AMU above those of the phosphorus oxides, corresponding to HPO, HPO_2, HPO_3 and HPO_4, were not clearly observed at the scan rate used.

TABLE IV Mass spectrometry of the phosphate A03 and A23 binders after heat treatment at 500 °C. Partial pressure (10^{-8} torr)

Atomic weight (AMU)	Possible formula	Phosphate A03	Phosphate A23
1	H	2	3
2	H_2	42	125
3	H_3	4	26
14	N	24	25
16	O	48	163
28	N_2	160	170
31	P	2	14
32	O_2/HP	33	42
47	PO	0	0.5
63	PO_2	0	0.8
79	PO_3	0	0.2
95	PO_4	0	0.1

The phosphate binders, after heat treatment at 500 °C, comprised aluminium metaphosphate (either type A or B) and extra phosphorus, probably in the form of phosphoric acid (H_3PO_4). The change of the heat treatment temperature from 500 °C to 800 °C caused the release of more phosphorus, thereby changing the P/Al ratio (EDS result, Table III) and the weight of the binder (TGA result, Figs 9 and 10). The released phosphorus was highest for the phosphate A23 binder and lowest for the phosphate A03 binder after changing the heat treatment temperature from 500 °C to 800 °C (Table III).

The acrylic emulsion dried at 100 °C had a smooth surface (according to SEM) and was amorphous (according to XRD). The water-glass binder showed a smooth surface with numerous small (1–3 μm) platelets on it after the 200 °C drying. After 1100 °C heating in air, the binder showed a rougher appearance, such

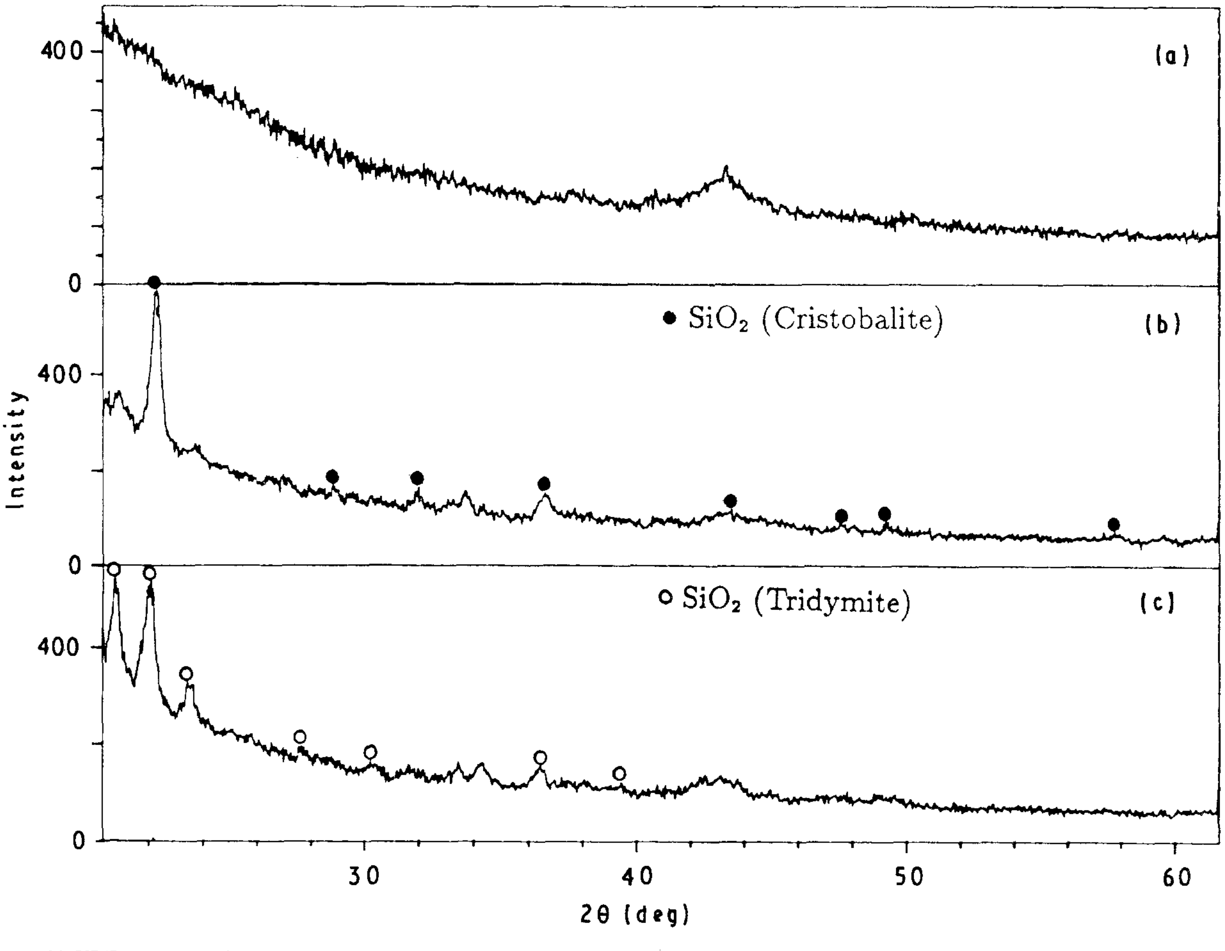

Figure 11 XRD patterns of the water glass after heat treatments at (a) 200, (b) 800 and (c) 1100 °C (in air).

that some pores (1–8 μm) were present. XRD patterns of the water-glass binder after heat treatment at 200, 800 and 1100 °C in air are shown in Fig. 11. Fig. 11a shows that the water-glass binder was largely amorphous after heat treatment at 200 °C. A crystalline phase emerged at 800 °C in air. The crystalline phase became clear after heat treatment at 1100 °C in air. The crystalline phase was identified as the tridymite SiO_2.

5. Discussion and conclusion

For discussion of these results, and conclusions, the reader is referred to the corresponding sections in Part III of this series [6].

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