

Review

Acid aluminum phosphate for the binding and coating of materials

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This is a review of acid aluminum phosphate for the binding and coating of materials. The acid aluminum phosphate in the form of a solution obtained by dissolving aluminum hydroxide in phosphoric acid, with a P/Al molar ratio of 23, is effective for the binding of fibrous or particulate materials. Porous ceramic articles are made using this binder by wet forming, followed by heat treatment. The binder resides at the junction of the adjacent fibers in the porous fibrous ceramic article. No free binder was observed in fibrous or particulate articles. The porosity is 45%–90% in fibrous articles, and is 25%–82% in particulate articles. Porosity above 61% in particulate articles is attained by adding carbon particles and subsequent removal of them by combustion. The binder proportion is 3–10 wt% in fibrous articles, and is ~0.1 wt% in particulate articles. Porous ceramic articles made using a silica binder instead of the acid aluminum phosphate binder are inferior in permeability, mechanical properties and creep resistance, and exhibit a wider pore size distribution. Free silica binder was observed in articles made with the silica binder. The acid aluminum phosphate with a P/Al ratio of 12 or 23 is also effective for coating materials, particularly graphite for the purpose of oxidation protection. © 2003 Kluwer Academic Publishers

1. Introduction

Acid aluminum phosphate refers to a liquid solution of phosphoric acid (H_3PO_4) and an aluminum salt (e.g., aluminum hydroxide), such that the proportion of acid is above that needed to form solid aluminum phosphate (e.g., $\text{Al}(\text{PO}_3)_3$, which is aluminum metaphosphate, and AlPO_4 , which is aluminum orthophosphate) [1]. Hence the P/Al molar ratio in acid aluminum phosphate is typically much higher than 3. Elements other than aluminum (e.g., calcium) can be used in acid phosphates [1], but aluminum is most commonly used, due to the wide availability of aluminum salts and the importance of aluminum and alumina (Al_2O_3) among engineering materials. Phosphoric acid itself can be used for the binding and surface modification of materials (e.g., ceramics) [2, 3], but the addition of aluminum significantly enhances the bonding ability [1, 4, 5].

The acid aluminum phosphate is to be distinguished from monoaluminum phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$), which is used in the form of solid particles or a water-based particulate slurry for binding ceramic particles in the fabrication of ceramic articles [6]. The viscosity of the slurry is much higher than that of the acid aluminum phosphate. A low viscosity is desirable for use in binding and coating. The acid aluminum phosphate binder is to be distinguished from aluminum phosphate binder, which has the P/Al molar ratio equal to 3 or less [7].

Heat treatment is needed subsequent to application of the acid aluminum phosphate in binding or coating. The heat treatment is partly for the purpose of drying and results in the formation of crystalline and amorphous aluminum phosphate solid phases, depending on the heating temperature and the possible interaction or reaction between the acid phosphate and the material to be bound or coated. Aluminum metaphosphate is a crystalline phase that is commonly formed after heating at 500–800°C [8].

The binding and coating of materials are central to the development and improvement of engineering materials. Binding refers to joining by using a material known as a binder. The fabrication of an article from particles or discontinuous fibers is commonly performed by the use of binder. The alternative method of sintering (without a binder) requires higher temperatures and is thus more expensive. A binder should be effective in binding, while not causing brittleness or, in the case of porous articles, impermeability. In general, the higher the proportion of binder used, the stronger, but the less permeable, is the resulting article. Thus, the binder technology is critical for articles that require permeability. The challenge is particularly large when permeability is required under the condition of small pore sizes, because small pores can be easily clogged by the binder. Thus, it is desirable for the binder to be effective in a

small proportion and that the binder does not reside in sites other than the points of joining among adjacent particles or fibers.

An additional challenge applies to binders for making materials that operate at high temperatures. Polymeric binders, such as polyvinyl alcohol, teflon and acrylic, cannot withstand temperatures above about 200°C. Conventional ceramic binders include oxysulfates, 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 [9]. The binders mentioned above are not suitable for making preforms, because, before the metal infiltration, the preform is typically heated up to 700–800°C, as in the case of the fabrication of aluminum-matrix composites. They are also unsuitable for making membranes for hot gas filtration. Binders such as silica colloid and acid aluminum phosphate are ceramic materials after heat treatment; they can withstand temperatures as high as 1000°C. However, silica and related glass binders have the tendency to undergo viscous deformation at high temperatures. The acid aluminum phosphate is superior to silica in the resistance to high temperatures, as described in Section 2.

Coating is commonly applied on a material for the purpose of improving the corrosion resistance, oxidation resistance, wear resistance and other properties. Coating processes involving spraying, dipping and related techniques of liquid or slurry application are inexpensive compared to those involving vacuum evaporation, sputtering and related thin film deposition techniques. The liquid or slurry in the former should have a low viscosity, so that the resulting coating conforms to the topography of the substrate.

This review addresses the use of the acid aluminum phosphate for the binding and coating of materials, though there has been much more work on binding than coating. In relation to binding, this paper includes comparison between the acid aluminum phosphate and the silica colloid, which is a widely used binder in ceramic processing. This review does not cover the following related topics: the use of oxides (e.g., aluminum oxide) with phosphoric acid in attaining bonding [10–12], phosphate conversion coatings on aluminum [13–17], aluminum phosphate gels [18–20] and molecular sieves [21, 22], aluminum phosphate catalysts [23, 24] and catalyst supports [25], monoaluminum phosphate and related non-acid phosphates [6, 26–28], alkyl acid phosphates [29, 30], calcium-aluminum phosphate [31], phosphate-oxalate inorganic-organic hybrid solids [32], and the digestion of phosphate rock with acids [33, 34].

2. Binder technology

A binder is used to bind particles or fibers together to form an article, whether the article is porous or

not. For non-porous articles, the binder is the matrix of the resulting composite material and is thus substantial in proportion. For porous articles, the binder is much smaller in proportion, so that the pores are not filled. As explained in Section 1, the performance of binders for porous articles is more demanding than that of binders for non-porous articles. Therefore, this section addresses porous articles. Due to the technical demand for binders that can withstand high temperatures, this section focuses on porous ceramic articles made by the use of binders for ceramics fibers as well as particles.

Porous ceramics are useful for filtration (e.g., hot gas filtration), diffusion (e.g., waste water treatment), dispersion rolls, ink pads for finger printing and preforms for the fabrication of ceramic reinforced metal-matrix composites by liquid metal infiltration. The porosity is above about 40% (as high as 90%) for all these applications, except for the preforms, the porosity of which can be as low as 25%. The low porosity of the preforms is due to the need for attaining a high volume fraction of the ceramic filler (as high as 75%) in the resulting metal-matrix composite in applications which require low thermal expansion (as needed for substrates, heat sinks and housing of microelectronics) and high modulus. The higher the ceramic filler volume fraction, the lower is the coefficient of thermal expansion and the higher is the modulus of the resulting metal-matrix composite.

The pore size of porous ceramics ranges from 0.1 to 50 μm . The greater the pore size, the higher is the permeability to fluids, whether liquids or gases. Permeability is required for all the applications mentioned above. However, a large pore size tends to be associated with low mechanical strength, due to the brittleness of ceramics. In addition, a large pore size is undesirable for the removal of small particles by filtration (as needed for hot gas filtration in the petrochemical industry) and for the dispersion of a liquid upon diffusion through the porous ceramic (as needed for waste water treatment, dispersion rolls and ink pads for finger printing).

The pore size of porous ceramics made by using binders is strongly affected by the unit size of the ceramic particles or fibers that make up the porous material. The larger the unit size, the larger is also the pore size. Hence, fine particles and fibers of small diameter and length are used for making porous ceramics with a small pore size. Uniaxial pressure applied during wet forming can be used to decrease the pore size, though the porous material becomes more anisotropic.

As fibers tend to be more expensive than particles, particles are more widely used than fibers. However, fibers are advantageous in providing more well-defined and spacious channels for a fluid to flow in the porous ceramic, thereby resulting in superior permeability. Furthermore, fibers are more effective than particles as a reinforcement, which is particularly important for preforms for making metal-matrix composites. On the other hand, fibers (unless oriented) are harder to be packed densely than particles, so the attainment of a low porosity is more difficult for fibers. The porosity tends to be higher for ceramics made from fibers than

those made from particles, thus resulting in superior permeability, but possibly inferior mechanical strength for the fibrous material.

Ceramic membranes are commonly in the form of a coating applied by spraying, dipping or other techniques on a substrate which has a larger mean pore size (hence higher permeability) and a higher mechanical strength. The membrane may be applied on an external or internal surface of the substrate, which may be in open tube, candle or other configurations.

Binders are most commonly in the form of a fine particle dispersion (preferably a colloid), as the small particle size facilitates distribution at the time of binder utilization. Examples are colloids of silica, alumina and monoaluminum phosphate. After application by wet forming, drying and appropriate heat treatment are needed. In the case of the silica colloid [9], the average size of the particles can range from under 10 nm to over 80 nm. A disadvantage of dispersions (even colloids) is the tendency of the particles to fill the open or continuous pores.

In contrast to the colloids or dispersions mentioned above, the acid aluminum phosphate is in solution form, thus allowing effectiveness for binding at even a small binder proportion and alleviating the problem of the filling of pores by the binder. The acid aluminum phosphate used in this paper for the sake of illustration is a solution of aluminum hydroxide in phosphoric acid. This solution was made at $\sim 150^{\circ}\text{C}$ with stirring [35]. Investigation of solutions with P/Al molar ratio of 1, 3, 6, 12 and 23 showed that the ratio of 23 is most effective [35]. The solution with the molar ratio P/Al of 1 could not be made because the fast chemical reaction resulted in the formation of a solid compound. The ratio P/Al for the monoaluminum phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) solution is 3. Thus, a P/Al ratio of 23 is used throughout this paper for the sake of illustration. This binder is designated A23. In wet forming, the binder is mixed with a liquid carrier (e.g., water, acetone, etc.). The less the binder proportion in the liquid, the smaller is the binder proportion in the resulting porous article.

X-ray diffraction analysis [35] showed that, when the A23 binder (by itself) was heat treated at 200°C , it remained in an amorphous form. Crystallization was shown to occur after heat treating the A23 binder to 500 or 800°C to form mainly type-A aluminum metaphosphate $\text{Al}(\text{PO}_3)_3$. After heat treating at 1100°C in air, the A23 binder became amorphous again. The amorphous phase was thought to be a metaphosphate glass [35]. After heating the binder at 1200°C in argon, the A23 binder was mainly amorphous, although a minor amount of a crystalline phase was also present. The minor crystalline phase was thought to be the cristobalite aluminum orthophosphate AlPO_4 [35].

3. The binding of fibrous materials

The A23 acid aluminum phosphate binder (4.1 wt%) was used with SiC whiskers (α -SiC, SILAR SC-9, Advanced Composites Materials Corp., $0.6\ \mu\text{m}$ diameter, 10–80 μm length, 80–90% whisker content) to make preforms (by water-based wet forming at a pressure

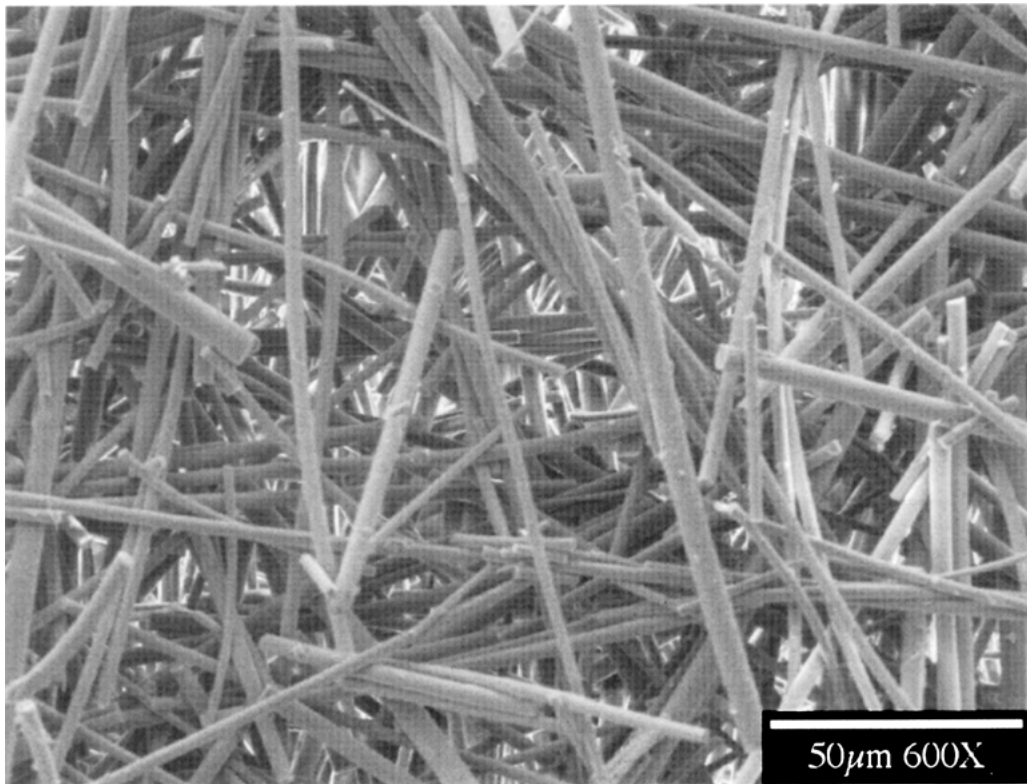
of 4.0 MPa, followed by drying at 200°C and then heat treatment in air at 500 or 800°C) for aluminum-matrix composites [35–37]. The SiC whisker preforms had a porosity of 78%. It was determined that (i) the crystalline binder phases (aluminum metaphosphate or aluminum orthophosphate), (ii) the binder-SiC reaction product (SiP_2O_7) and (iii) the binder-Al reaction product (AIP) after heat treating offered protection to the SiC whiskers, since the reaction between SiC and aluminum was reported to be harmful [38]. It was demonstrated that silicon phosphate (SiP_2O_7) acted as an in-situ binder and was responsible for increasing the compressive strength of the preform.

The A23 acid aluminum phosphate binder (3 wt%) was used with SiC whiskers (β -SiC, Tokai Carbon, Japan) to make preforms (by wet forming) for magnesium-matrix composites [39, 40]. The whisker-matrix interfacial reaction product MgO was distributed evenly at the interface, such that a definite orientation relationship existed between MgO and SiC, as shown by transmission electron microscopy. In contrast, MgO was distributed unevenly in various parts of the composite when the silica binder was used in place of the acid aluminum phosphate binder [39].

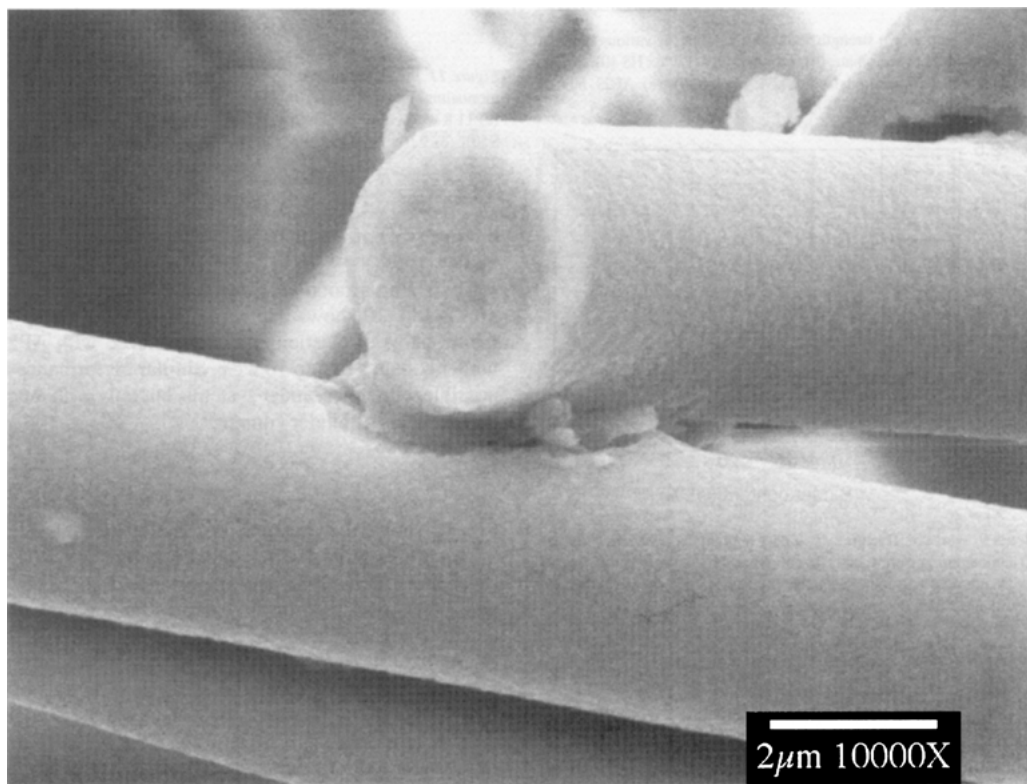
The A23 binder (1.9 wt%) was used with carbon fibers (isotropic-pitch-based, unsized, 10 μm diameter, $\sim 100\ \mu\text{m}$ length, Carboflex P-100, Ashland Petroleum Co.) to make preforms (by water-based wet forming at a pressure of 1 MPa, followed by drying at 200°C and heat treatment in argon at 800°C) for aluminum-matrix composites [36]. The carbon fiber preforms had a porosity of 40–50%.

The A23 binder (9.5 wt%) was used with alumina fibers (Saffil, ICI Performance Chemicals, Cheshire, UK; RF milled, 3 μm mean diameter, 115 μm mean length, 3.3 g/cm^3 density, 1–2 GPa tensile strength, δ -alumina) to make membranes by water-based wet forming (with 1 part of binder to 15 parts of water, and filtration of the slurry through a 200 mesh stainless steel screen) and subsequent heat treatment (placing in a pre-heated 300°C furnace, increasing the temperature to 800°C at a rate of $20^{\circ}\text{C}/\text{min}$ and then holding at 800°C for 3 h), with pressure (10.5 or 17.5 kPa) optionally applied during wet forming to control the density [41–43]. The membranes had a porosity of 90%.

The use of the A23 acid aluminum phosphate binder in place of a commercial silica colloid binder in the fabrication of the alumina fiber membrane results in improved creep resistance (as tested under compression at 600 and 800°C), increased flexural strength (as tested up to 800°C), increased storage modulus and damping capacity (as tested up to 500°C), and decreased thermal conductivity (as tested at 600 and 800°C), in addition to increased permeability and compressive strength (0.65 MPa) at room temperature [41–43]. In particular, the permeability of the membrane made with the A23 binder is about four times that of the membrane made with the silica colloid binder. Table I compares the properties of the two membranes. Note the narrow pore size distribution attained by the use of the A23 binder. As shown by scanning electron microscopy (Fig. 1), the acid aluminum phosphate binder resides only at the



(a)



(b)

Figure 1 Scanning electron micrograph of (a) an alumina fiber membrane with the acid phosphate binder at 9.5 wt% binder content and (b) the acid phosphate binder bonding the junction of two fibers.

junction of adjacent fibers [41]. In contrast, free binder particles are present in the case of the silica binder.

4. The binding of particulate materials

The A23 acid aluminum phosphate binder (0.1 wt%) was used with AlN (3.7 μm mean), SiC (3.0 μm mean)

and Al₂O₃ (3.0–3.5 μm average) particles to make preforms (by wet forming at 0–39 MPa, followed by drying at room temperature and then heat treatment at 510°C for 3 h) for aluminum-matrix composites [44, 45]. The particle preforms had a porosity of 35%–45%, as controlled by the pressure applied during wet forming. The

TABLE I Summary of results for alumina fiber filter membranes using acid aluminum phosphate and silica binders [41–43]

	Phosphate	Silica
Pore size for >80% of the pores (μm)	2–4	0.35–5.0
Flexural strength (MPa) at room temperature	2.2	1.7
Flexural strength (MPa) at 800°C	1.9	1.5
Creep compressive strain (800°C, 500 min)	0.04%	0.5%
Storage modulus (GPa) at 500°C and 5 Hz	0.7	0.3
Thermal conductivity (W/m · K) at 600°C	0.10	0.16
Smallest detected pore pressure (kPa)	37 ± 2	138
Smallest detected pore diameter (μm)	1.24 ± 0.06	0.33 ± 0.08
Mean flow pore pressure (kPa)	17 ± 0.9	9.6
Mean flow pore diameter (μm)	2.6 ± 0.1	4.8 ± 0.2
Bubble point pressure (kPa)	2.0 ± 0.1	1.31
Bubble point diameter (μm)	26 ± 1	35 ± 2
Diameter at maximum pore size distribution (most common pore)	2.42	0.35
Average Darcy air permeability constant, k (10^{-9} cm ²)	114 ± 6	30 ± 4

TABLE II Effect of applied pressure (during wet forming) on the AlN volume fraction of the resulting preform

Applied pressure (MPa)	Vol% AlN
0	55
7.8	58–59
2 × 7.8	60.5
3 × 7.8	61.5
4 × 7.8	62.3
5 × 7.8	65.3

higher the applied pressure, the lower was the porosity and the greater was the particle volume fraction, as shown in Table II for the case of AlN particles [44]. No binder was observed distinctly by scanning electron microscopy (Fig. 2), due to its low proportion (0.1 wt%).

The use of a commercial silica colloid binder in place of the A23 acid aluminum phosphate binder resulted in binder precipitation in the liquid carrier (water or acetone), high viscosity in the particle slurry, surface cracks in the preforms during heat treatment, low compressive strength in the preforms, and incomplete infiltration of liquid aluminum into the preforms during aluminum-matrix composite fabrication (i.e., poor permeability) [44].

The liquid carrier used in wet forming was acetone instead of water in the case of AlN particles, because AlN reacts with water. The higher the binder/carrier ratio, the higher was the compressive strength of the resulting preform, but the lower was the permeability. The highest compressive strength attained in permeable particulate preforms with 45% porosity was 5 MPa, as obtained by using AlN particles, the A23 binder, and acetone as the carrier (binder/acetone ratio = 1/45) [44]. At a binder/acetone ratio of 1/10, the resulting preform was not sufficiently permeable, due to the blockage of channels in the preform by the excess binder [44]. In the absence of a carrier, the compressive strength was exceptionally low, in spite of the high binder content. This is because of the reaction of AlN with the undiluted binder and the consequent gaseous porosity in the AlN preform.

The A23 acid aluminum phosphate binder (<0.16 wt% in the resulting preform) was used with a mixture of SiC particles (3–5 μm) and carbon particles (20 μm mean) to make SiC preforms (by wet forming at 1.8 MPa, followed by drying at room temperature and then 120°C, and subsequent oxidation treatment in oxygen at 750°C for the purpose of removing the carbon portion of the preform by combustion) for aluminum-matrix composites [46]. The porosity of the preforms

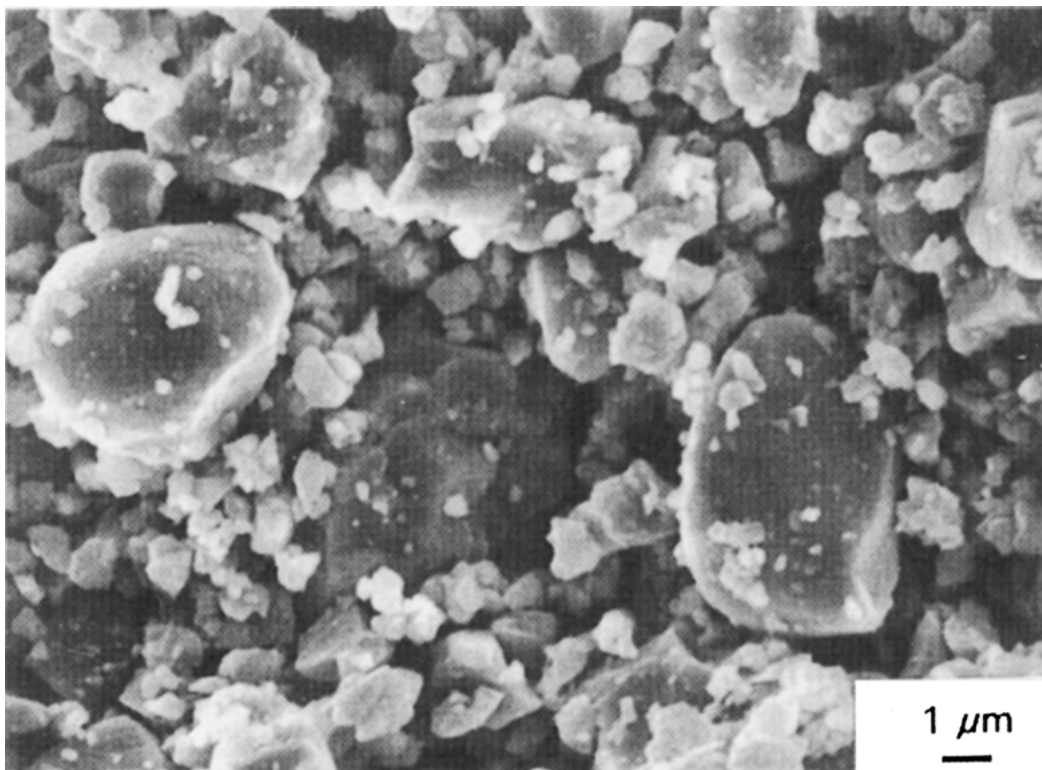


Figure 2 SEM micrograph of an AlN preform fabricated with a carrier/binder ratio of 45:1 and baked at 510°C.

ranged from 61% to 82%, as controlled by the ratio of SiC and carbon used. The high porosity, as made possible by the carbon particles which were burnt out, is attractive for making metal-matrix composites with a low particulate volume fraction (thereby composites that are not as brittle as those with a high particulate volume fraction).

The A23 acid aluminum phosphate binder (~0.1 wt%) was used with silicon particles (1–5 μm) to make preforms (by wet forming at 5 MPa, followed by drying at 200°C and heat treatment at 400°C for 4 h) for aluminum-matrix composites [47]. The porosity of the preforms was 50%. By using aluminum-silicon alloys for the liquid metal infiltration, the silicon particles in the preforms were partially dissolved by the liquid alloy. The remaining silicon particles, together with the silicon contributed by the Al-Si alloy matrix, resulted in a silicon network within the composite after solidification.

The A23 acid aluminum phosphate binder (~0.1 wt%) was used with nickel particles (3–7 μm) to make preforms (by wet forming at 5 MPa, followed by drying at 200°C, heat treatment at 400°C for 4 h and then sintering in vacuum at 1050°C for 1 h) for aluminum liquid infiltration [48]. The preforms had a porosity of 42% before sintering and 22% after sintering. The reactive infiltration of liquid aluminum into the sintered preform resulted in nickel aluminide Ni_3Al in a single phase form. The reactive infiltration of liquid aluminum into the preform without sintering resulted in an aluminum-matrix NiAl_3 particle composite.

5. The coating of materials

Calcium phosphate [49–51] and chromium phosphate [52, 53] coatings are applied to metals (e.g., aluminum and titanium) for corrosion protection and enhancement of adhesion to organic coatings. Aluminum orthophosphate (AlPO_4) coating obtained by reaction of aluminum chloride and phosphoric acid (i.e., $\text{AlCl}_3 + \text{H}_3\text{PO}_4 \rightarrow \text{AlPO}_4 + 3\text{HCl}$) on glass for the purpose of attaining optical effects and enhancing chemical and abrasion resistance [54]. Less common is the use of the acid phosphate for coating.

The acid aluminum phosphate is applied on carbon materials (particularly graphite) for the purpose of oxidation protection [55]. The A23 acid aluminum phosphate and the acid aluminum phosphate with $P/\text{Al} = 12$ are both effective for the oxidation protection of carbon materials, provided that the carbon materials have been treated with ozone (for forming oxygen-containing functional groups on the surface of the carbon) prior to coating. Without the ozone treatment, the impregnation is not effective. With the ozone treatment, the impregnation causes surface coating, which is more complete when the acid content is higher (A23). The use of phosphoric acid without aluminum hydroxide for coating carbon degrades the oxidation resistance of the carbon, due to the formation of oxygen-containing functional groups. Table III shows the oxidation resistance of carbons in terms of the temperature (during heating in air at 10°C/min) at which the weight loss is

TABLE III Oxidation resistance of carbons as indicated by the temperature (during heating at 10°C/min) at which the weight loss is 10%

Treatment	Graphite	Carbon fiber
As received	750°C	450°C
Impregnated with A23 acid aluminum phosphate ^a	760°C	550°C
Ozone treated, then impregnated with A23 acid aluminum phosphate ^a	1375°C	825°C
Ozone treated, then impregnated with acid aluminum phosphate with $P/\text{Al} = 12^a$	1375°C	865°C
Impregnated by H_3PO_4 in the absence of $\text{Al}(\text{OH})_3$	/	440°C

^aImpregnation was followed by heating to 800°C in N_2 for 20 min.

10%. For the same treatment, the fibers are less oxidation resistant than the graphite, but the treatments have similar effects on fibers and graphite. X-ray diffraction shows that the coating (while in color) is type-A aluminum metaphosphate, $\text{Al}(\text{PO}_3)_3$, for the graphite that has been ozone treated and then impregnated with the A23 acid aluminum phosphate.

The less critical role of phosphoric acid in coating than in binding is consistent with the diminished requirement on the P/Al ratio for coating than for binding. The formation of an impervious coating is not needed for binding, but is required for oxidation protection.

6. Conclusion

The acid aluminum phosphate in the form of a solution obtained by dissolving aluminum hydroxide in phosphoric acid, with a P/Al molar ratio of 23 rather than 12, is effective for the binding of fibrous or particulate materials. Porous ceramic articles for use as membranes and composite reinforcement preforms are made using this binder by wet forming, followed by heat treatment, which results in aluminum metaphosphate in most cases. The binder resides at the junction of the adjacent fibers in the porous fibrous ceramic article. No free binder was observed in fibrous or particulate articles. The porosity is 45%–90% in fibrous articles, and is 25%–82% in particulate articles. Porosity above 61% in particulate articles is attained by adding carbon particles and subsequent removal of them by combustion. The binder proportion is 3–10 wt% in fibrous articles, and is ~0.1 wt% in particulate articles. Porous ceramic articles made using a silica binder instead of the acid aluminum phosphate binder are inferior in permeability, mechanical properties and creep resistance, and exhibit a wider pore size distribution. Free silica binder was observed in articles made with the silica binder. The acid aluminum phosphate with a P/Al molar ratio of 12 or 23 is also effective for coating materials, particularly graphite for the purpose of oxidation protection.

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