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Processing of Nextel 720/mullite composition composite using electrophoretic deposition

W. S. WESTBY, S. KOONER*, P. M. FARRIES, P. BOOTHER, R. A. SHATWELL
Structural Materials Centre, MSS, Griffith Building, DERA, Farnborough, GU14 0LX, UK
E-mail: skooner@dera.gov.uk

A technique for electrophoretic deposition of alumina, silica and alumina/silica mixtures has been developed. Experiments have been carried out to successfully infiltrate these matrices into electrically non-conducting Nextel 720 2D alumina fibre weave. Surfactants based on carboxylic acid/amine combinations in ethanol were assessed. The objective was to enable the co-deposition of alumina and silica at mullite ratio by tailoring the electrophoretic mobility. Tartaric acid with dibutylamine was identified as the most efficient surfactant mix. Aluminium and silicon contents were measured by atomic emission spectrometry, ensuring that a deposit of mullite composition had been achieved. The distribution of species within samples was monitored via elemental mapping in SEM. Fibres were heat treated in air at 1400 °C to assess tolerance to proposed sintering temperatures. Resultant composite green bodies are densely infiltrated with powder deposited within fibre tows. The ease of preparation of low volume content powder suspensions reduces slurry processing time in comparison to conventional routes. The infiltration time required is short. These findings indicate that a potentially economic electrophoretic composite manufacturing route, not restricted to single powder species or conductive fibre weaves, has been developed.

1. Introduction

Continuous fibre reinforced ceramic composities are candidate materials for certain gas turbine components. However, their use is not yet widespread due to prohibitive processing costs and the instability of fibre properties at elevated temperature. Oxide matrix-oxide fibre composites are being developed specifically for high temperature applications in oxidising environments, but have tended to utilise single crystal Saphikon[†] fibre [1]. The advent of the newly developed Nextel[‡] 720 fibres has provided an oxide fibre system capable of sustaining 1200 °C but at a significantly lower cost [2].

This paper describes the processing of a Nextel 720 fibre reinforced mullite composition matrix composite produced by electrophoresis. The novel aspect of this work is the electrophoretic co-deposition of alumina and silica ceramic powders at mullite ratio without segregation into a non-conductive fibre weave. The advantages over a conventional slurry route are reduced processing times due to the use of low concentration ceramic suspensions and improved control over green body microstructure.

Composite systems for 1400 °C and above will require the next generation of mullite fibres but may be processed by the techniques developed with the Nextel 720 system.

1.1. Materials

Mullite provides superior high temperature creep resistance to alumina and is more resistant to thermal shock [3]. The present work, therefore focuses on the processing of a mullite composition matrix composite reinforced with Nextel 720 fibres giving thermomechanical matching of fibre and matrix.

Nextel 720 fibres are produced via a sol-gel route and result in crystalline α-alumina and mullite [2]. These 12 μm diameter fibres have a tensile modulus of 260 GPa and a tensile strength of 2100 MPa. Their mechanical properties are acceptable for turbine engine applications up to 1200 °C and short excursions to 1300 °C are tolerated [4].

Interface development within alumina/mullite systems has concentrated on porous and layered oxides. Oxide coatings applied by CVD on to silicon carbide monofilaments have been investigated at DERA [5].

The exact phase composition of the matrix system should be tailored to the application. In the case of composite systems for 1200 °C, it is sufficient to have an alumina/aluminosilicate matrix allowing lower processing temperatures than would be required to guarantee mullite formation and thus preserving fibre properties.

1.2. Electrophoresis

Traditional processing routes for fibre reinforced ceramics include:

[†] Saphikon Inc.
[‡] 3M Corporation.

*Author to whom all correspondence should be addressed.

- slurry infiltration followed by hot pressing which limits shaping capability,
- chemical vapour infiltration (CVI) which is expensive due to the number of re-infiltration steps and capital cost of equipment,
- reaction bonding which results in significant porosity.

A more cost effective route would be slurry infiltration followed by low pressure sintering. To facilitate the use of lower pressure during sintering, the ceramic matrix composite (CMC) green body must be sufficiently dense and more importantly, homogeneous [6]. Electrophoretic infiltration of powders has potential for producing such green bodies.

Electrophoresis is the process by which charged particles in a liquid medium move under an applied potential. If a fibre preform is substituted for the deposition electrode and the suspension is of the required ceramic matrix powder, a CMC green body can be manufactured. In the case of non-conductive fibres, such as Nextel 720, the fibre weave is placed in front of the deposition electrode and the deposit forms on the electrode and around the fibres.

In a polar liquid, particles develop a charge whose sign and magnitude depend on the interaction between the surface and the liquid surrounding it. pH can have a large effect if hydrogen ions play a part. This surface charge, for reasons of neutrality, must then be balanced by oppositely charged ions and results in the formation of a double layer around the particle [7]. When an electric potential is applied to charged particles, they move and there is shear within the double layer. The potential at this shear plane is known as the zeta potential. The electrophoretic mobility of the particle is defined by Smoluchowski's equation:

$$\text{Electrophoretic Mobility} = \frac{U}{X} = \frac{\varepsilon\zeta}{4\pi\eta} \qquad (1)$$

where U = velocity, X = field strength, ε = dielectric constant, ζ = zeta potential, and η = viscosity.

A suitable suspension for electrophoretic infiltration should have:

- high particle surface charge to increase the mobility of the ceramic particles,
- high dielectric constant of the liquid phase,
- low viscosity to increase particle mobility,
- low conductivity of the suspending medium to minimise solvent transport.

A high particle surface charge generally gives greater suspension stability due to repulsive forces between particles.

The surface charge of the particles may be engineered by the addition of surfactants to give a high charge and the required sign. Surfactants should be clean burning because they will be retained in the green body.

Deposition occurs at either the anode or cathode depending on the sign of the charge on a particle. If co-deposition of two different particle species is required, the species must have the same sign of surface charge. The suspension must also be designed so that the desired ratio of the species is obtained. If the electrophoretic mobility of the two species is roughly equal, a green body can be made from a suspension containing the required species ratio whereas a dissimilar electrophoretic mobility will lead to phase segregation.

Electrolysis of the liquid phase may occur at the same time as electrophoretic deposition. The suspending medium must be chosen to avoid the production of gases at the depositing electrode which may disrupt the formation of the green body. The selection of liquid phase and particle adsorbent must be tailored to obtain dense and uniform deposition.

Infiltration into a porous structure has been investigated by Gal-Or *et al.* [8] and has been shown to be enhanced by high field strength, high powder content in the suspension and high particle mobility. However, with time there is a build-up of surface deposit preventing further penetration. Most of the work to date has involved some form of coating process [8, 9] or the production of monoliths [10]. In all cases this involves a simple deposition process and not infiltration. Recently however, electrophoresis has been used to fabricate SiO_2 matrix composites [11] and it is here that the problem of infiltration versus deposition is highlighted, i.e. there is residual porosity within the fibre preform because the surface deposit inhibits full infiltration.

2. Experimental background

2.1. Process development

Ethanol was chosen as the suspending medium. Electrolysis produces ethane at the cathode and ethanal which oxidises to ethanoic acid at the anode. The anode was selected for deposition because gases are not formed here. The production of negatively charged alumina and silica particles was therefore necessary.

2.1.1. Alumina

Surfactants containing a carboxylic acid and an amine were tested. Chemical formulae for the species referred to in this section are given in the Glossary.

This type of surfactant was chosen because it is clean burning and will not leave a residue in the material when it is sintered. Surfactant optimisation was carried out to ensure a high electrophoretic mobility, enabling rapid infiltration of the fibre weave.

A surface charge can be created on alumina particles by protonation of surface hydroxyl groups (OH^-) or exchange of the OH^- group for a different group such as a citrate ion (Cit^{3-}) [12]. These competing reactions mean that the sign of the alumina surface charge will be determined by pH.

$$\mathrm{AlOH} + \mathrm{H_3O^+} \leftrightarrow \mathrm{AlOH_2^+} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{AlOH} + \mathrm{HCit^{2-}} \leftrightarrow \mathrm{AlCitH^-} + \mathrm{OH^-} \qquad (3)$$

Citric acid and triethylamine have been used successfully by other workers to produce a negative surface charge on alumina in ethanol [6]. A negative surface charge will be produced by the adsorption of a citrate

TABLE I Data from handbook of chemistry and physics, 74th edition

	Temperature (°C)	Step	pK
Citric acid	20	1	3.14
	20	2	4.77
	20	3	6.39
α-Tartaric acid	25	1	2.98
	25	2	4.34

ion only if it contains more than one COO^- group. The presence of triethylamine will promote the removal of a hydrogen ion from more than one of the carboxylic acid groups which would otherwise be suppressed in ethanol. Hidber *et al.* [12] have studied the citrate-alumina surface complex in water using ATR-FTIR spectroscopy.

Achieving complete dissociation of all three carboxylic acid groups present in citric acid is problematic because as each successive proton is removed further deprotonation becomes increasingly difficult. This is demonstrated by the successively increasing pK values for the three carboxylic acid groups (see Table I). Complete dissociation is desirable, because it would maximise the negative surface charge at each adsorption site.

$$H_3Cit + N(CH_2CH_3)_3 \leftrightarrow H_2Cit^- + (CH_3CH_2)_3NH^+ \qquad (4)$$

$$H_2Cit^- + N(CH_2CH_3)_3 \leftrightarrow H_2Cit^{2-} + (CH_3CH_2)_3NH^+ \qquad (5)$$

$$HCit^{2-} + N(CH_2CH_3)_3 \leftrightarrow Cit^{3-} + (CH_3CH_2)_3NH^+ \qquad (6)$$

An amine with a high basicity used in conjunction with the carboxylic acid maximises deprotonation of the acid groups. A series of amines with alkyl groups of increasing size were tested in addition to triethylamine. As the size and number of alkyl groups increases, the basicity of the amine should increase because the greater electron donating effect will enhance the stability of the amine cation. The cation is also stabilised by maximising solvation. Secondary amines were therefore used because solvation of tertiary amines is sterically hindered in water [12]. It was assumed that this would also apply to amines in ethanol. Whilst steps were taken to maximise the acid dissociation, it is unlikely that significant quantities of Cit^{3-} ions were generated as the dielectric constant of ethanol is much less than that of water and acid dissociation constants are typically 10^5 times smaller in ethanol than water.

Tartaric acid was investigated as an alternative to citric acid because it is a smaller molecule. Therefore, it should be possible to pack a greater number of tartrate ions (Tar) onto an alumina particle.

$$H_2Tar + N(CH_2CH_3)_3 \leftrightarrow HTar^- + (CH_3CH_2)_3NH^+ \qquad (7)$$

$$HTar^- + N(CH_2CH_3)_3 \leftrightarrow Tar^{2-} + (CH_3CH_2)_3NH^+ \qquad (8)$$

2.1.2. Silica

Silica is known to have a negative charge in water above pH 7 but reacts with alcohols to form an esterified surface, although it is reported that the presence of small amounts of water considerably reduces the degree of esterification [13]. The negative charge on silica in water is thought to arise from either surface ionisation of silanol groups or hydroxyl ions occupying spaces in the open structure of the surface [13].

$$SiOH + ROH \leftrightarrow SiOR + H_2O \qquad (9)$$

$$SiOH + H_2O \leftrightarrow SiO^- + H_3O^+ \qquad (10)$$

The addition of a small amount of water to the ethanol was considered necessary to obtain a negative charge on the silica.

2.2. Deposition

Before attempting to co-deposit alumina and silica, the rate of deposition from single species suspensions was measured. A large difference between the deposition rates of the two species would be a disadvantage when carrying out co-depositions.

A 3 : 2 molar ratio of alumina to silica is required to make stoichiometric mullite. Co-depositions were carried out on a flat plate before any infiltration experiments, so that the suspension could be tailored to deposit the correct bulk alumina to silica ratio.

2.3. Infiltration

Single species infiltrations were carried out prior to mixed species infiltrations, to determine whether infiltration of the non-conducting weave could be accomplished with the individual alumina and silica species.

For mixed species infiltration an evenly distributed, aggregate free deposit is desirable. Mullite formation will be faster if the powders are intimately mixed. Silica aggregates formed in the deposits, so surfactants were tested with the aim of preventing the formation of these aggregates.

In non-aqueous suspensions coagulation is prevented by ionic repulsion or steric stabilisation [14]. Ionic repulsion seemed the most appropriate stabilisation mechanism because steric stabilisation is usually achieved with high molecular weight substances, which may leave voids when they are burnt off. Glutamic acid and aspartic acid were identified as two potential ionic surfactants, which could be added without causing excessive interference with the chosen surfactant for alumina. Glutamic acid and aspartic acid are acidic amino acids which contain one amine group and two carboxylic acid groups. If the correct pH is obtained it should be possible to produce a zwitterion containing one NH_3^+ group and two COO^- groups. Adsorption of the NH_3^+ group onto the silica negative surface may be possible, cancelling out the positive charge and leaving two negative COO^- groups, thereby effectively doubling the charge at the adsorption site and increasing ionic repulsion.

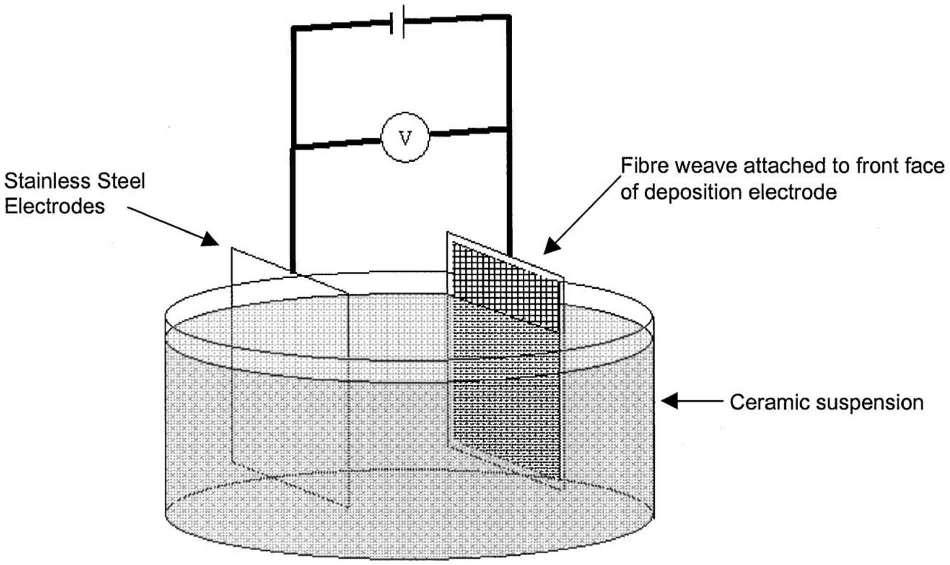


Figure 1 Composite manufacture using electrophoretic deposition.

Work carried out following the investigation of glutamic acid and aspartic acid indicated that a non-ionic surfactant might be more appropriate. Various commercially available non-ionic surfactants (in this case fatty alcohol ethoxylates) follow the general formula $CH_3(CH_2)_m(CH_2CH_2O)_nH$. A fatty alcohol ethoxylate will be soluble in ethanol if the ratio of 'm' to 'n' is correct. The presence of the OH group at the end of the molecule should make hydrogen bonding with surface SiOH groups possible. 2-(2-butoxyethoxy)ethanol was chosen because of its low molecular weight.

2.4. Fibre-ageing

It is intended that the oxide-oxide composite green bodies produced by electrophoretic infiltration should be densified by pressureless or gas pressure sintering. This high temperature processing route is considered cheaper than hot-pressing and can allow near net shape component manufacturing. In contrast to hot-pressing however, high temperatures are required to achieve theoretically dense ceramic matrix material. The feasibility of the electrophoretic production method is critically dependant on the availability of a fibre with sufficient thermal resilience to withstand sintering at up to 1400 °C and to go on to perform in service. Thus, one of the initial steps in this investigation was to age the Nextel 720 fibre weaves in air at 1400 °C for 24 h.

3. Experimental

3.1. Suspensions

Suspensions were made to 5 vol % using an ultrasonic horn (20 kHz) to break up solid aggregates. The suspension medium was ethanol in all cases. Two alumina powder grades have been used: A1[§] and A2[¶], which are 0.5 and 0.9 μm in diameter respectively. The A2 powder has a greater green density and increased magnesia content to aid sintering. A single amorphous silica powder was chosen for easy sintering[*] and used in all cases. Processing time was 15 min in the case of single and mixed species suspensions.

The ceramic powders were characterised by use of a Matec Applied Sciences' Electrokinetic Sonic Analysis System^{TM} [15] to determine iso-electric point and optimise surfactant content. This apparatus consists of a probe with parallel electrodes across which an alternating voltage is applied. When used within a ceramic suspension, the charged ceramic particles between the electrodes oscillate generating a sound wave. The amplitude of this sound wave is measured (electronic sonic amplitude, ESA) and is proportional to dynamic mobility and zeta potential. The ESA can be continually monitored during surfactant addition or titration.

3.2. Fibres

The Nextel 720 fibres were used in 8 harness, satin weave form. The warp and fill count is [11] yarns/mm. Desizing was carried out by heat treating the fibres at 600 °C in air.

To assess the tolerance of the fibres to typical sintering temperatures a series of ageing experiments were conducted. Fibres were held in mullite tubes to minimise contamination and held at temperature in air for up to 24 h.

3.3. Electrophoretic infiltration

Fig. 1 shows the basic configuration of the electrophoretic cell. The electrodes were stainless steel plates, with the fibre weave attached to the anode. Deposition conditions were 100 V, with a gap of 1.6 cm between electrodes i.e. a mean field strength of 62.5 V/cm, applied for up to 7 min in constant voltage mode.

[§] Baco RA207LS alumina, Alcan.

[¶] AES 21, Sumitomo, Japan.

[*] Microsilica, Elkem, Vaagsbygd, Norway.

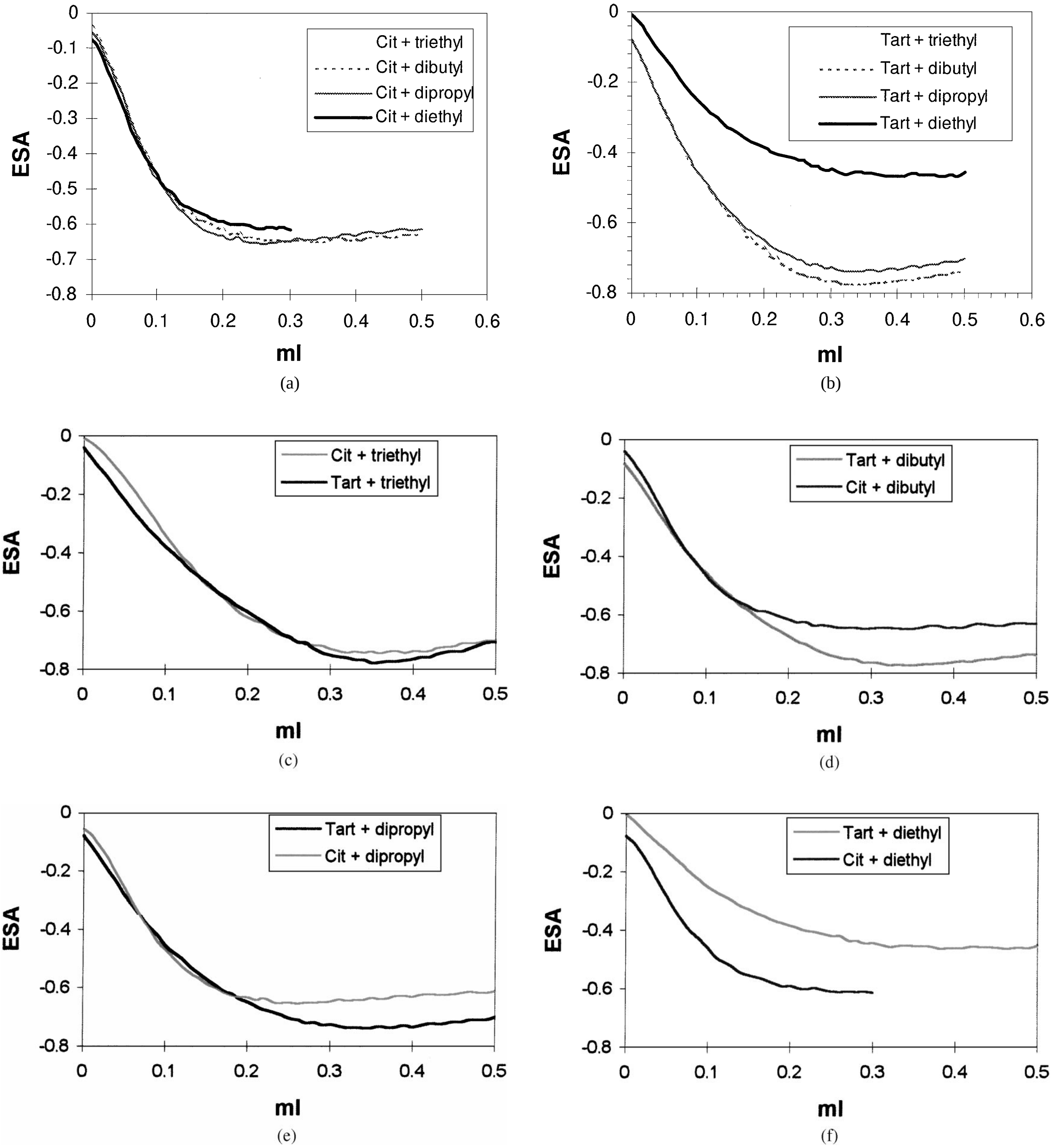


Figure 2 The effect of using different surfactants on the ESA of A1 alumina (a) citric acid with amines (b) tartaric acid with amines. The effect of using different surfactants on the ESA of A1 alumina-citric and tartaric acid with (c) triethylamine, (d) dibutylamine, (e) dipropylamine and (f) diethylamine.

3.4. Green body evaluation and chemical analysis

In the case of monolithic samples, flakes of the green body were mounted on SEM stubs for microstructural evaluation. Where the green body was in composite form, specimens were infiltrated with Caldofix^{TM} low viscosity resin, then sectioned and polished.

Elemental mapping was conducted using a Leica Stereoscan 360^{TM} scanning electron microscope with EDX analyser.

Analysis for Al and Si in co-deposited samples was carried out when the bulk alumina to silica ratio was required. 0.1 g portions of each deposit were fused with lithium tetraborate at 1100 °C and the product was dissolved in dilute hydrochloric acid. An ARL 3410^{TM} ICPAES (inductively coupled plasma atomic emission spectrometer) was used to analyse the solutions. The analysis method was based on draft BS method DD ENV 955-4:1997.

Transmission electron microscopy was carried out on a Philips EM 400^{TM} (120 kV). Sample preparation involved ion thinning at a 4° incidence angle in a PIPS using a 3.5 kV argon gun. X-ray diffraction involved scanning the samples using Cu radiation at 40 kV, 40 mA over the range 15°–90° 2θ using a step size of 0.02° and count time per step of 10 s. Analysis of the data was carried out using Bruker AXS Diffrac software and the ICDD powder diffraction database.

TABLE II Surfactant compositions

Surfactant	Surfactant composition (main constituent ethanol)
A	0.5M citric acid/2M triethylamine (16 vol % water)
B	0.5M citric acid/2M diethylamine (16 vol % water)
C	0.5M citric acid/2M dipropylamine (16 vol % water)
D	0.5M citric acid/2M dibutylamine (16 vol % water)
E	0.5M tartaric acid/1.5M triethylamine (16 vol % water)
F	0.5M tartaric acid/1.5M diethylamine (16 vol % water)
G	0.5M tartaric acid/1.5M dipropylamine (16 vol % water)
H	0.5M tartaric acid/1.5M dibutylamine (16 vol % water)

4. Results and discussion

4.1. Surfactant optimisation

4.1.1. Alumina

Eight surfactants containing citric acid or tartaric acid in combination with either triethylamine, diethylamine, dipropylamine or dibutylamine were made (the composition of the surfactants is given in Table II and chemical names in Section 6). The behaviour of 5 vol % A1 alumina suspensions containing these surfactants was characterised by measuring electrokinetic sonic amplitude. Graphs displaying volume of surfactant added versus ESA are given in Fig. 2. Suspensions containing tartaric acid generally had a higher magnitude ESA than those containing citric acid (Fig. 2c–e), but tartaric acid in combination with diethylamine was an exception (Fig. 2f). The ESA was also affected by the amine used. Surfactants containing dibutylamine or triethylamine gave the highest magnitude ESA, followed by dipropylamine then diethylamine (Fig. 2a and b).

The generally higher electrophoretic mobility of alumina with tartaric acid surfactants indicates that the smaller molecule size is probably an advantage, as assumed. However, tartaric acid combined with diethylamine gave a lower ESA than citric acid combined with diethylamine. An explanation for this result has not been found. The maximum negative ESA of the alumina also increased as the alkyl chain length of the secondary amines increased regardless of which acid was used (Fig. 2a and b), so an increase in basicity did appear to result in a higher degree of ionisation of the carboxylic acid groups. Roughly the same ESA was obtained when tartaric acid/dibutylamine and tartaric acid/triethylamine surfactants were used (Fig. 2b), but a more negative ESA was obtained when citric acid/triethylamine was used instead of citric acid/dibutylamine (Fig. 2a). Tartaric acid may be fully dissociated when combined with dibutylamine, but it appears that further protons can be removed from citric acid if triethylamine is used (the increase in ESA could be due to the presence of citric acid molecules containing three COO^- groups). Triethylamine is apparently a stronger base in ethanol than dibutylamine, therefore the liquid phase did not affect the basicity of the amines as predicted in Section 2.1.2.

Tartaric acid with dibutylamine (surfactant H) was used as the surfactant for subsequent work, because it gave the most negative ESA at the lowest concentration. 0.7 ml of this surfactant is required to achieve maximum electrophoretic mobility in 300 ml of 5 vol % A1 alumina.

4.1.2. Silica

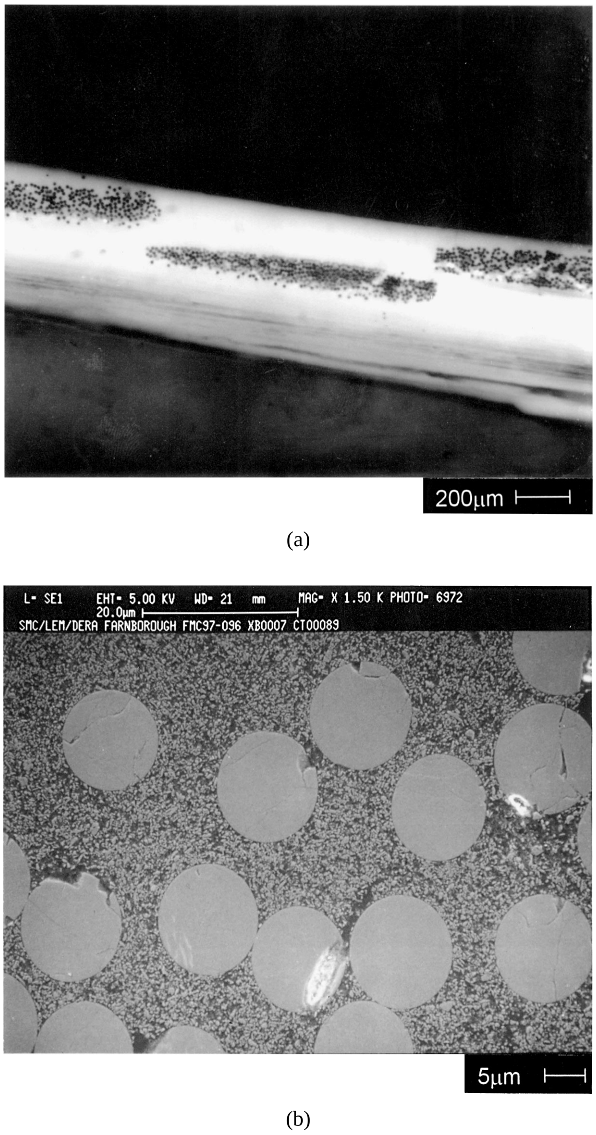
Depositions of silica from a 5 vol % Silica ethanol suspension were carried out in the presence of 2 vol % water with and without surfactant H added, and from a suspension containing surfactant but no extra water. A thick silica deposit rapidly formed at the positive electrode in all cases. The addition of water was unnecessary, possibly because the water already present in the suspension was enough to prevent esterification or excess amine present in the surfactant prevented the esterification reaction.

$$\mathrm{SiOH} + \mathrm{Bu_2NH} \leftrightarrow \mathrm{SiO^-} + \mathrm{Bu_2NH_2^+} \qquad (11)$$

4.2. Electrophoresis

4.2.1. Single species infiltration

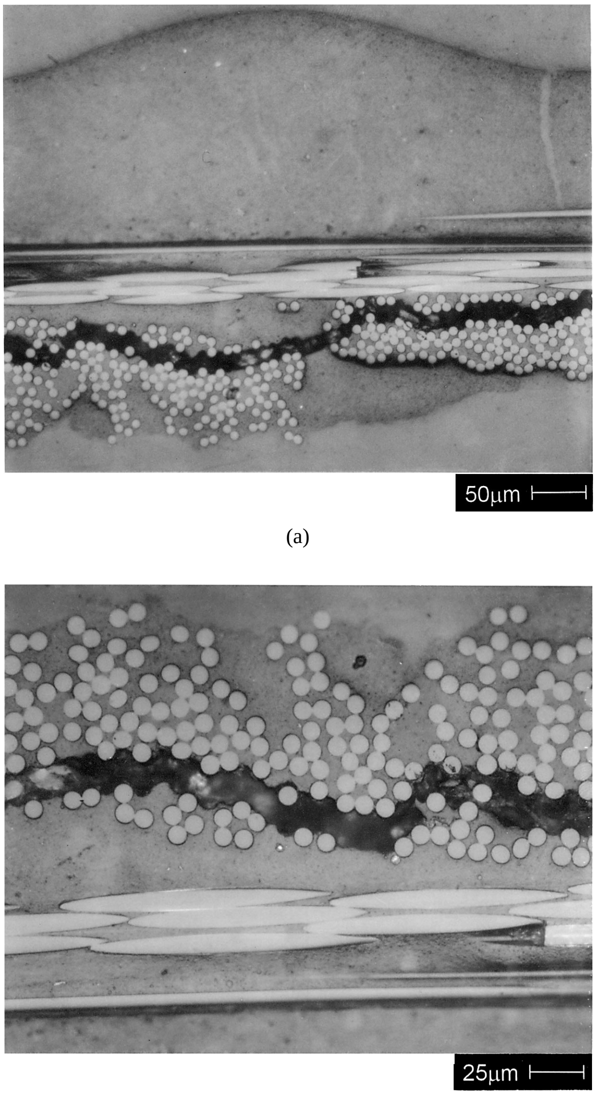
Nextel 720 weave was infiltrated with alumina giving a homogeneous distribution of ceramic powder around fibres with the occasional void, Fig. 3a. The deposition time was 2 min, and considering the reduced suspension preparation time, this technique compares favourably



(a)

(b)

Figure 3 (a) Optical micrograph of A1 alumina infiltration (Mag. ×50) and (b) SEM micrograph of A1 alumina infiltration (Mag. ×1500).



(a)

(b)

Figure 4 Optical micrograph Nextel 720 weave infiltrated with silica (a) Mag. ×200 and (b) Mag. ×400.

with traditional wet processing techniques. Full infiltration has been achieved with a non-conductive weave suggesting that the optimisation of the electrophoretic cell has been successful, Fig. 3b.

Infiltration of Nextel 720 weave with silica was more rapid resulting in a thick surface deposit, Fig. 4a. Cracks were visible and may be attributable to drying or damage caused on separation of green body from the deposition electrode. However, again there was full infiltration, even at the tightest points within fibre bunches (Fig. 4b), with no voids present.

4.2.2. Rate of deposition in single species suspensions

The rate of deposition was investigated with monolithic depositions. Timed depositions were carried out on weighed electrodes from 5 vol % suspensions at a fixed potential difference and electrode separation. The deposits were left to dry and the electrodes were reweighed. An approximate deposition rate was calculated in g min^{-1} cm^{-2}. Alumina A1 deposited at a rate of 0.04 g min^{-1} cm^{-2} and silica at 0.06 g min^{-1} cm^{-2}. Deposition of both alumina and silica was rapid and thick deposits formed in under two minutes.

4.2.3. Co-deposition of alumina and silica

Initial co-depositions of alumina and silica were carried out using alumina A1 and silica. The work was continued using alumina A2 and silica. Alumina A1 was replaced with alumina A2 because A2 is easily sinterable due to higher magnesia content. After each co-deposition, the deposit was analysed by ICPAES for Al and Si to determine whether or not the desired ratio had been achieved.

The silica deposition rate was higher than that of alumina, but not greatly so. The effect of mixing the two species was unknown, therefore the first co-deposition attempted was from a suspension with a 3 : 2 molar ratio of alumina to silica (3.66 vol % A1 alumina, 1.34 vol % silica). The green body formed had a mean molar ratio of 3.1 : 2 alumina to silica. Two further depositions were carried out from a fresh suspension, replacing alumina A1 with alumina A2 (3.56 vol % A2 alumina, 1.44 vol % Silica). The deposits contained a mean molar ratio of 3.4 : 2 alumina to silica. There was no apparent difference in the bulk composition of the two deposits, the deposition process appears repeatable with the same suspension. The full results of the ICPAES analysis are given in Table III.

Further suspension optimisation was unnecessary because the molar ratio of alumina to silica was considered acceptably close to 3 : 2. The molar ratios obtained

TABLE III Alumina:silica molar ratios achieved on deposition

Suspension	Deposition sequence	Molar ratio $Al_2O_3 : SiO_2$
3.66 vol % A1 alumina, 1.34 vol % silica	First	3.12 : 2
3.66 vol % A1 alumina, 1.34 vol % silica	First	3.13 : 2
3.56 vol % A2 alumina, 1.44 vol % silica	First	3.37 : 2
3.56 vol % A2 alumina, 1.44 vol % silica	First	3.47 : 2
3.56 vol % A2 alumina, 1.44 vol % silica	Second	3.42 : 2
3.56 vol % A2 alumina, 1.44 vol % silica	Second	3.34 : 2

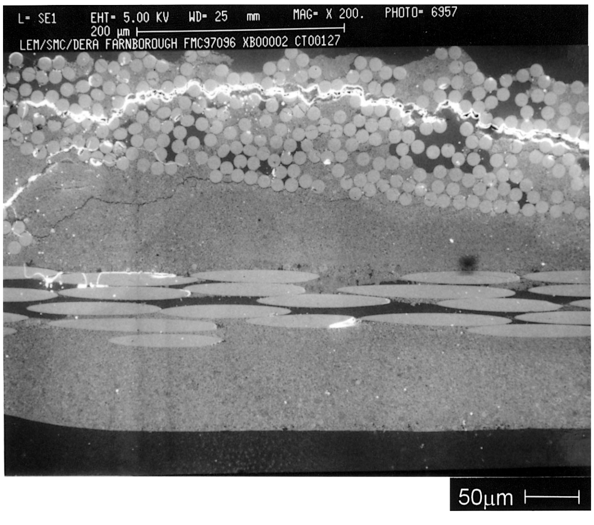


Figure 5 SEM micrograph A1 alumina and silica co-infiltrated (Mag. ×200).

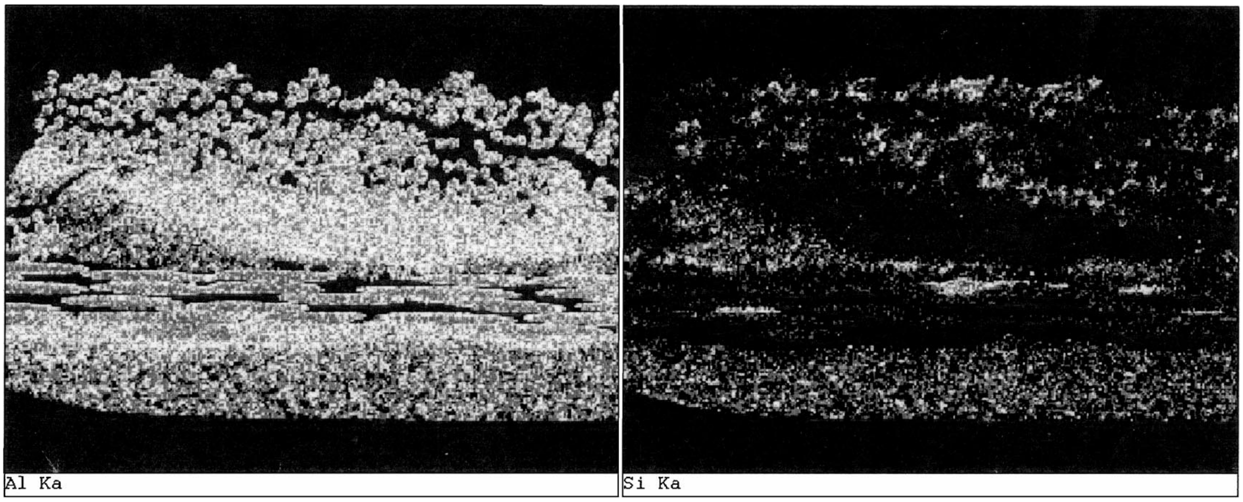


Figure 6 Elemental map for Al and Si from Fig. 5.

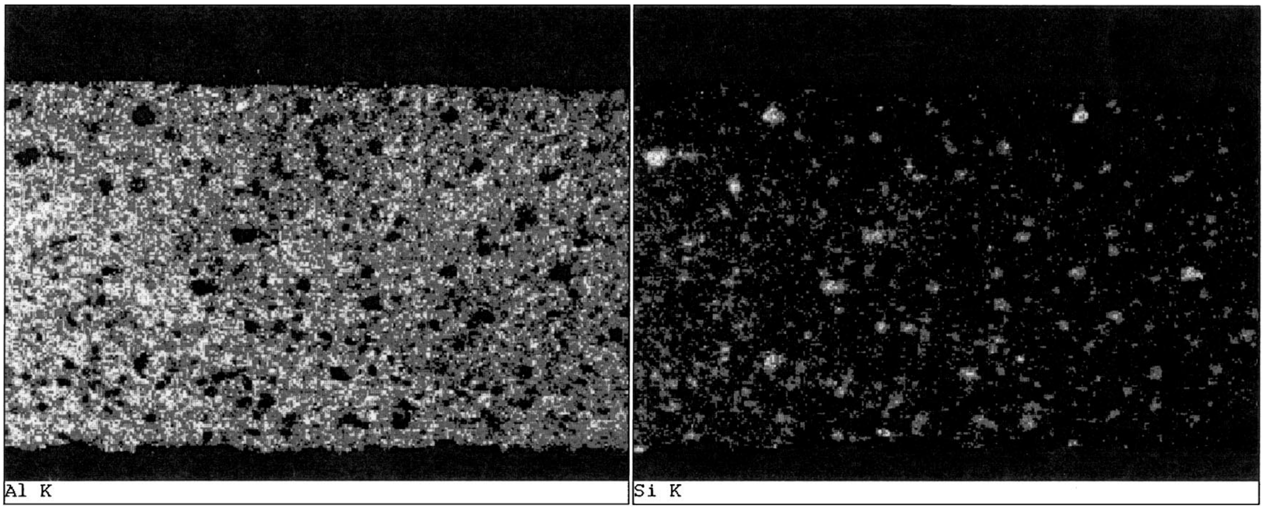


Figure 7 Elemental map for Al and Si of monolithic deposition using A2 alumina (Mag. ×200).

indicate that the rate of deposition of both species changed when the species were mixed. Either the species interact or the surfactant is affected by mixing the species. The alumina content increased when alumina A2 was used instead of alumina A1. The increase in alumina content cannot be explained by an increase in surface area (A1 has a surface area of 7 m^2 g^{-1}[†] and A2 is 3.5–4 m^2 g^{-1}) but may be attributed to its greater density and size.

4.2.4. Mixed infiltration

Infiltration of one layer of Nextel 720 weave was carried out using both mixed species suspensions. The infiltrations were rapid and were completed in less than seven minutes. The weaves were set in epoxy resin and cross sections examined by optical microscopy and SEM. Elemental maps of the infiltrated weaves and one flat plate deposit were obtained using SEM-EDX (energy dispersive X-ray microanalysis). Large drying cracks were observed in the weave and infiltration was extensive but not complete (see Fig. 5). The elemental maps show some segregation of alumina and silica and silica aggregates of the order of 10–20 μm had formed, Fig. 6. Silica aggregates were also seen in the weaveless deposit, Fig. 7.

4.2.5. Prevention of silica aggregate formation

Four mixed surfactants were made, two containing glutamic acid/tartaric acid/dibutylamine and two containing aspartic acid/tartaric acid/dibutylamine. The compositions are given in Table IV. The surfactants contained either a 1 : 1 or a 1 : 1.25 molar ratio of amine groups to carboxylic acid groups. Four mixed alumina A2 and silica suspensions were made and a different mixed surfactant was added to each. A deposit was formed on a flat plate from each suspension. The dry deposits were analysed by ICPAES and elementally mapped.

The deposits all contained silica aggregates and there did not appear to be a reduction in their number or size.

[†] A1 data from Baco data sheet, A2 properties measured by Mandoval Ltd.

TABLE IV Surfactant compositions with aspartic and glutamic acids

Surfactant	Surfactant composition (main constituent ethanol)
I	0.5M tartaric acid, 1.5M dibutylamine, 0.5M aspartic acid (21 vol % water)
J	0.5M tartaric acid, 1.5M dibutylamine, 0.5M glutamic acid (21 vol % water)
K	0.5M tartaric acid, 2M dibutylamine, 0.5M aspartic acid (21 vol % water)
L	0.5M tartaric acid, 2M dibutylamine, 0.5 M glutamic acid (21 vol % water)

Three deposits had an increased alumina content. The deposit produced using 0.5M glutamic acid, 0.5M tartaric acid and 1.5M dibutylamine had the same alumina to silica ratio as the slurry. Table V displays the full results of the ICPAES analysis.

TABLE V ICPAES analysis results

Amino acid surfactant used	Molar ratio $Al_2O_3 : SiO_2$
K	3.99 : 2
K	3.95 : 2
L	3.94 : 2
L	3.94 : 2
I	3.95 : 2
I	3.91 : 2
J	3.29 : 2
J	3.29 : 2

The raised alumina content of three deposits implies that either the rate of alumina deposition had increased or that the rate of silica deposition had decreased. This would be possible if the amino acid had a

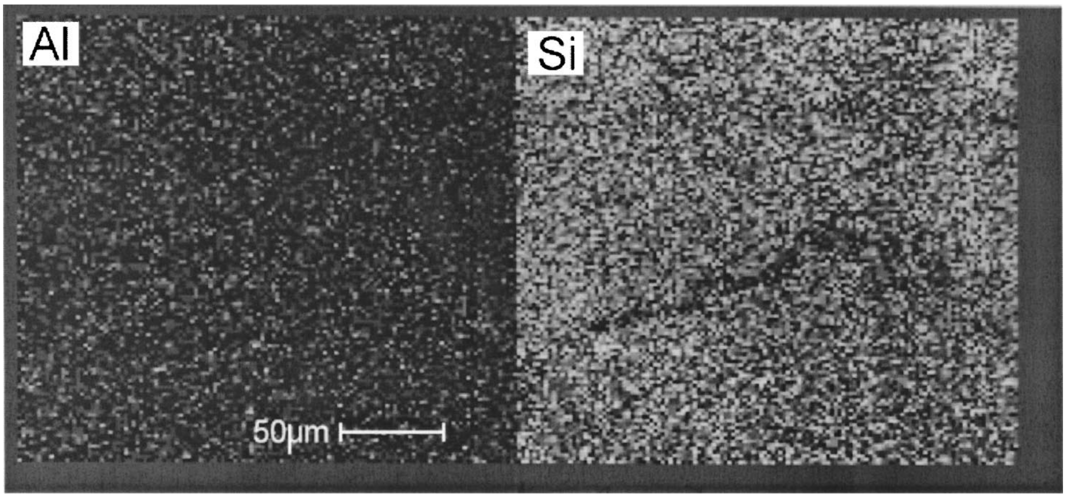


Figure 8 Elemental map of Al and Si for dried suspension of A2 alumina and silica (Mag. ×300).

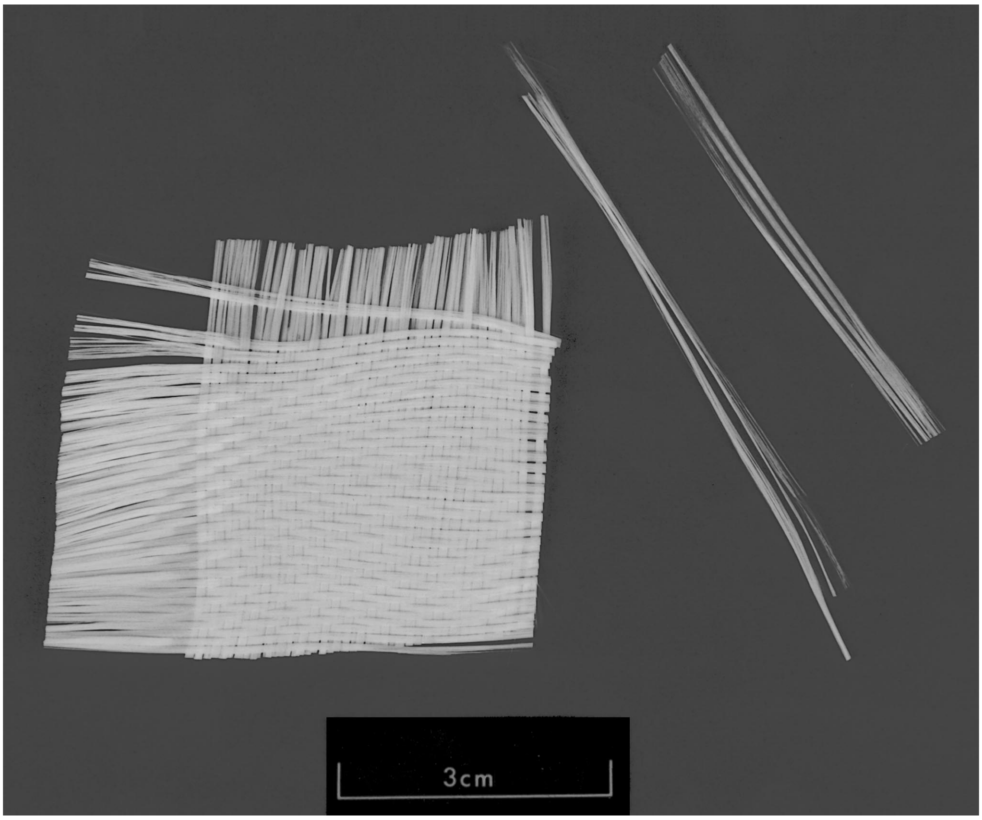
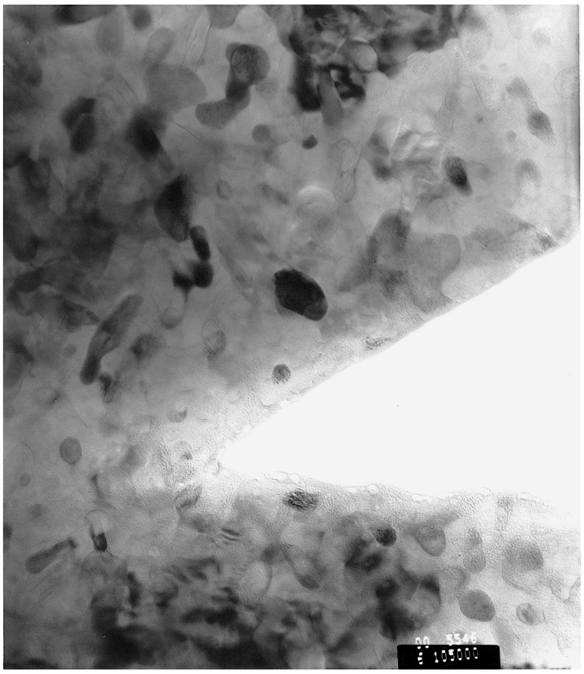


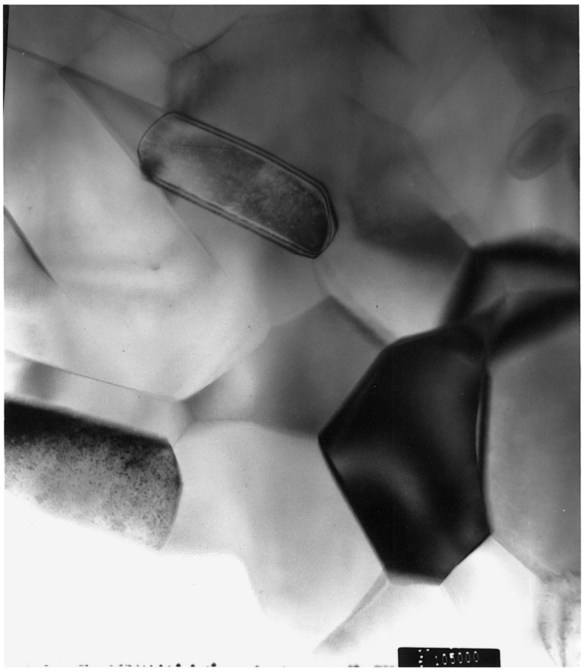
Figure 9 Nextel 720 fibre tow and weave after ageing at 1400 °C in air (as received fibres shown on right of picture).

double negative charge or a single positive charge, indicating that the zwitterion was probably absent. Therefore the deposit with the undisturbed alumina to silica ratio was the only one that may have been affected by zwitterions, but as mentioned previously this still contained silica aggregates.

The site of formation of the silica aggregates was unknown. They could be present in the suspension or they could be forming on the electrode. This problem was resolved by dropping a small quantity of suspension onto an SEM stub, evaporating the ethanol and elementally mapping the dried mixed powder (see Fig. 8). No silica aggregates were observed. The aggregates in the electrophoretic deposits probably form when the silica comes into contact with the electrode, possibly due to loss of surface charge. The use of a non-ionic surfactant to sterically stabilise the silica therefore seemed appropriate if a suitable low molecular weight substance could be identified.



(a)



(b)

Figure 10 TEM micrograph of (a) as-received Nextel 720 fibres (Mag. ×105,000) and (b) aged Nextel 720 fibres (Mag. ×105,000).

The chosen non-ionic surfactant (2-(2-butoxyethoxy) ethanol) was added to a mixed silica and alumina A2 suspension in stages and a deposition was carried out at each stage. Elemental maps of the dry deposits were produced. The addition of 2-(2-butoxyethoxy)ethanol did not prevent the formation of the silica aggregates.

4.3. Fibre-ageing

Experiments have been conducted where desized fibre has been aged at 1400 °C for up to 24 h. It was found that there was very little difference in appearance when compared to the as-received fibres, Fig. 9. XRD results showed little difference in composition. However, TEM examination revealed appreciable grain growth over time, with up to a 15-fold increase in grain size, Fig. 10a and b. This would translate to a decrease in strength and modulus.

Other workers have found a 20% fall in tensile strength when fibres are held at 1200 °C to 1500 MPa [2] which is still within acceptable limits for most applications. Short excursions up to 1350° during composite processing i.e. with matrix protection, have shown no significant fall in tensile strength and modulus [4].

This suggests that processing temperatures of below 1400 °C should be used to ensure that fibre properties are maintained. However, this will not produce a mullite matrix. A trade-off of fibre properties for matrix stability is necessary within this composite system. The exact phase compositions will then be decided by application requirements.

5. Conclusions

Electrophoretic deposition has been shown to be a successful technique for ceramic composite processing. The suspension preparation route is simple and deposition rates are extremely rapid at less than 7 min per weave.

It has been demonstrated that electrophoretic deposition can be successfully used to infiltrate non-conductive Nextel 720 fibre weave. Green body microstructures are dense and the flaw concentration is low. It is thought that the use of ultrasonics and controlled drying will decrease the number of flaws present still further. The optimisation of surfactants enables two species infiltration resulting in green bodies with minimal phase segregation.

Thus, by using this processing technique, it is possible to produce high quality Nextel 720/mullite composition matrix green bodies which can be consolidated to form mullite-mullite composites.

6. Glossary

Citric acid	$HOOCCH_2C(OH)COOHCH_2COOH$
Tartaric acid	$HOOCCH(OH)CH(OH)COOH$
Triethylamine	$N(CH_2CH_3)_3$
Diethylamine	$HN(CH_2CH_3)_2$
Dipropylamine	$HN(CH_2CH_2CH_3)_2$
Dibutylamine	$HN(CH_2CH_2CH_2CH_3)_2$
Glutamic acid	$HOOCCH_2CH_2CHNH_2COOH$
Aspartic acid	$HOOCCH_2CHNH_2COOH$
Ethanal	CH_3CHO
Ethanoic acid	CH_3COOH
2-(2-butoxy-ethoxy)ethanol	$CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$

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