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Processing of Nextel™ 720/mullite composition composite using electrophoretic deposition

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Abstract

A technique for electrophoretic deposition (EPD) of alumina, silica and alumina/silica mixtures has been developed. These matrices have been successfully infiltrated into electrically non-conducting 2D alumina fibre weaves. Surfactants based on carboxylic acid/amine combinations in ethanol were assessed. The objective was the co-deposition of alumina and silica at mullite ratio by tailoring electrophoretic mobilities. Aluminium and silicon contents were measured by inductively coupled plasma atomic emission spectrometry. The distribution of species within samples was monitored via elemental mapping in scanning electron microscopy (SEM). Fibres were heat treated in air at 1400°C to assess tolerance to proposed sintering temperatures. Sintering studies were carried out at 1400 and 1600°C on powder compacts containing alumina and silica in the mullite ratio. The effect of seeding the compacts with mullite was investigated with the aim of reducing the temperature required for mullite formation. 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. Intermediate amounts of a fine mullite type powder seeding encouraged mullite formation when compacts were sintered at 1400°C for 2 h. These findings indicate that a potentially economic electrophoretic composite manufacturing route, not restricted to single powder species or conductive fibre weaves, has been developed. Crown Copyright © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Aluminosilicate fibres; Composites; Electrophoresis; Mullite; Sintering

1. Introduction

Continuous fibre reinforced ceramic composite materials have potential uses as certain gas turbine components but widespread application is currently limited 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] Newly developed Nextel™ 720 oxide fibres (3M Corporation) provide a system capable of sustaining 1200°C at a significantly lower cost.[2] Composite systems for 1400°C and above will require the next generation of mullite fibres, but may be processed using techniques developed with the Nextel 720 system. The development and processing of a mullite composition matrix composite reinforced with Nextel 720 fibre by electrophoresis is described. The electrophoretic co-deposition of mixed ceramic powders without segregation, into a non-conductive fibre weave is a novel technique. Processing times are reduced through the use of low concentration ceramic suspensions. Improved control over green body microstructure is possible in comparison to processing via a conventional slurry route.

1.1. Materials

The thermal shock of resistance of mullite is superior to that of alumina.[3] 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 up to 1200°C and short excursions to 1300°C are tolerated.[4] The present work focuses on the green processing of a mullite composition matrix composite reinforced with Nextel 720 fibres and investigation of the densification

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and transformation of a matrix composed of separate alumina and silica powders. Fibres and matrix are thus thermomechanically matched. The precise phase composition of the matrix should be tailored to the targeted application. Composite systems destined for operation at 1200°C should perform adequately with an alumina/aluminosilicate matrix, precluding the need for higher processing temperatures which would damage fibre properties.

1.2. Electrophoresis

Traditional processing routes for fibre reinforced ceramic composites each have associated drawbacks. Slurry infiltration followed by hot-pressing is suitable for production of only a limited range of component shapes. Chemical vapour infiltration (CVI) is expensive due to the large number of re-infiltration steps required and the capital cost of the equipment. Reaction bonding results in significant porosity. Slurry infiltration followed by sintering would lead to a lower cost material. To facilitate the use of lower pressure during sintering, the ceramic matrix composite (CMC) green body must be dense and more importantly, homogeneous.[5] Electrophoresis, the process by which charged particles in a liquid medium move under an applied voltage, has the potential for producing such greenbodies. If a fibre preform is used as 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.

The development of an electric double layer on a solid particle surface is described by DLVO theory[6] and the behaviour of charged particles on the application of an electric potential described by Smoluchowski's equation for electrophoretic mobility:

$$\text{Electrophoretic mobility} = \frac{U}{X} = \frac{\varepsilon\zeta}{4\pi\eta} \tag{1}$$

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.

The sign of the charge on the particle surfaces determines whether anodic or cathodic deposition occurs. If co-deposition of separate species is required, surface properties must be tailored to give them the same sign of surface charge. Further, the effects of different particle electrophoretic mobilities on the deposition ratio should be considered. Deposit composition is controlled by engineering equal mobilities and depositing from a suspension of the desired component ratio. Differing particle mobilities could 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.[7] and high field strength, high powder content in the suspension and high particle mobility have been demonstrated to enhance infiltration. However, with time surface deposits build up preventing further particle penetration. The majority of the work to date has involved some form of coating process[7,8] or the production of monoliths.[9] In all cases this involves a simple deposition process, not infiltration. Recently however, electrophoresis has been used to fabricate SiO_2 matrix composites[10] and the problem of infiltration versus deposition has been highlighted, i.e. there is residual porosity within the fibre preform because the surface deposit inhibits full infiltration.

2. Experimental

2.1. Surfactants

Alumina and silica powders were suspended in ethanol and surfactants were added to modify particle mobility. The behaviour of alumina suspensions with various surfactants containing a carboxylic acid and an amine was characterised.[11] The highest electrophoretic mobility (and thus stability) of the alumina suspension at 5 vol% powder was achieved by adding a surfactant composed of 0.5 M tartaric acid/1.5 M dibutylamine (16 vol% water).

2.2. Deposition and infiltration

Single and then dual species depositions of alumina (Alcan Baco RA207LS or Sumitomo AES21,) and silica (Elkem Microsilica) were initially made onto a flat plate electrode to quantify the relative deposition rates of alumina and silica. Bulk deposits were analysed for alumina and silica ratio to allow the tailoring of the two component suspension. Elemental mapping by energy dispersive X-ray (EDX) microanalysis in SEM was used to test for segregation.

Similarly, single species infiltrations into Nextel 720 fibre weaves were carried out prior to mixed species infiltrations. For mixed species infiltrations evenly distributed, aggregate free deposits are desirable. Mullite formation will be accelerated and promoted by intimately mixed powders.

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.

2.3. 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. While providing a cost effective route and the capability for near net-shape forming, higher temperatures are required to achieve theoretically dense ceramic matrix material than when hot-pressing. 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.

2.4. Sintering

Pressed mixed powder discs have been sintered at 1400 and 1600°C. Mullite was added to a selection of the powder compacts to determine whether seeding would assist mullite formation. Two different mullite powders were used, KCM sintered mullite 73 (particle size 0.00–0.08 mm) and a 1 μm mullite, denoted F1.[12] Imsil A8 silica and AES21 alumina were used throughout, but some powder mixes were also made using Elkem microsilica to compare the effect of different silica starting powders. XRD indicates that F1 mullite is an aluminosilicate and may in fact be a mullite precursor. XRD was used to determine amounts of mullite present in sintered compacts.

Experience of Sacks et al.[13] suggests that while densification of alumina/silica powder compacts is possible at 1400°C, a separate mullitisation step, initiated by heat treatment to 1500 or 1600°C was necessary. These workers have shown, however, that seeding compacts of silica coated alumina particles with 2 wt% of an extremely fine mullite powder (median particle size ~0.15 μm) mullite powder results in almost complete conversion to mullite at 1400°C.

3. Results and discussion

3.1. Electrophoresis

3.1.1. Single species infiltration

Alumina was infiltrated into a Nextel 720 weave producing a homogenous distribution of ceramic powder around the fibres with occasional voids. Full infiltration

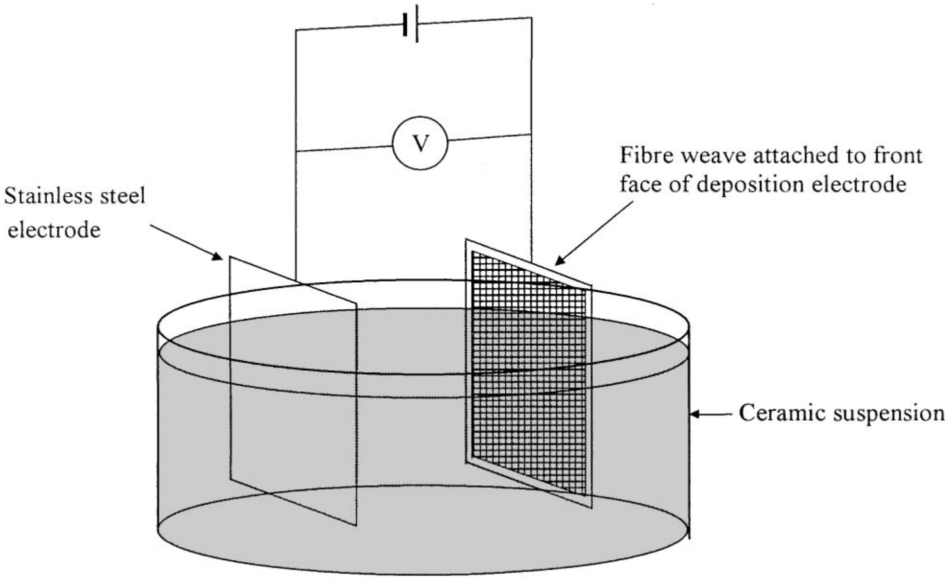

Fig. 1. Composite manufacture using electrophoretic deposition.

was achieved in 2 min. Infiltration of a Nextel 720 weave with silica was more rapid and resulted in a thick, surface powder deposit. However, full infiltration, even of tight points in the weave was still achieved.

The rates of deposition of the individual species were investigated with monolithic depositions. The deposition rates of dry matter were calculated as 0.04 $g.min^{-1}$ cm^{-2} for Alcan Baco RA207LS alumina and 0.06 $g\,min^{-1}$ cm^{-2} for the silica. Deposition of both alumina and silica was rapid and thick deposits formed in less than 2 min.

3.1.2. Co-deposition of alumina and silica

Initial co-depositions of alumina and silica were carried out using the Alcan alumina. Later AES21 alumina from Sumitomo was substituted. This product is more easily sinterable due to its higher magnesia content. After each co-deposition, the product was analysed for Al to Si ratio by inductively coupled plasma atomic emission spectroscopy (ICPAES).

The silica deposition rate was higher than that of alumina, but not greatly so. The effect of mixing the two species was unknown, therefore co-deposition was first attempted from a suspension with a 3:2 molar ratio of alumina to silica (3.66 vol% Alcan 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 Alcan with Sumitomo alumina (3.56 vol% AES21 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 1.

Further suspension optimisation was unnecessary because the molar ratio of alumina to silica was considered acceptably close to 3:2. The molar ratios obtained 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 AES21 alumina was used instead of Baco RA207LS alumina. The increase in alumina content cannot be explained by an increase in surface area (Baco RA207LS has a surface area of 7 m^2 g^{-1} and AES21 is 3.5–4 m^2 g^{-1}) but may be attributed to its greater density and size.

3.1.3. 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. Some drying cracks were observed in the weave and infiltration was extensive but not complete (see Fig. 2). The large crack in the centre of the sample has been attributed to the epoxy curing stage and steps are taken to eliminate it in later work. The elemental maps show some segregation of alumina and silica and silica aggregates of the order of 10–20 μm had formed (Fig. 3). Silica aggregates were also seen in the monolithic deposit (Fig. 4).

3.1.4. 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 2. The surfactants contained either a 1:1 or a 1:1.25 molar ratio of amine groups to carboxylic acid groups. Four mixed AES21 alumina 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. Three deposits had an increased alumina content. The deposit produced using 0.5 M glutamic acid, 0.5 M tartaric acid and 1.5 M dibutylamine had the same alumina to silica ratio as the slurry.

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.

The site of formation of the silica aggregates was unknown. They could be present in the suspension or

Table 1
Alumina:silica molar ratios achieved on deposition

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

they could be forming on the electrode. This question was resolved by dropping a small quantity of suspension onto an SEM stub, evaporating the ethanol and elementally mapping the dried mixed powder. 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.

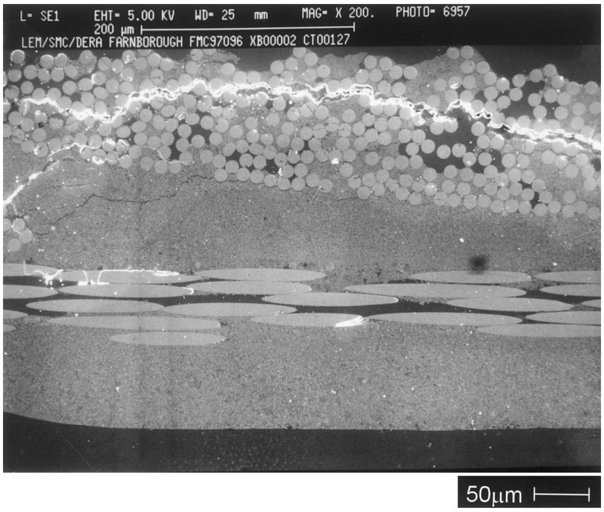

Fig. 2. SEM micrograph A1 alumina and silica co-infiltrated (mag.×200).

The chosen non-ionic surfactant [2-(2-butoxyethoxy) ethanol] was added to a mixed silica and alumina 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.

Trials were conducted using two silica powders, Acematt HK400 and Imsil A8 which have larger particles than the Elkem microsilica, in an attempt to prevent aggregate formation. Acematt HK400 was difficult to handle, formed low density deposits and produced larger silica aggregates from a mixed suspension than the Elkem microsilica. Imsil A8, however formed deposits similar to those seen with Elkem microsilica and elemental mapping indicated that the silica deposits formed on deposition are smaller than those formed with Elkem microsilica. Elemental analysis by ICPAES

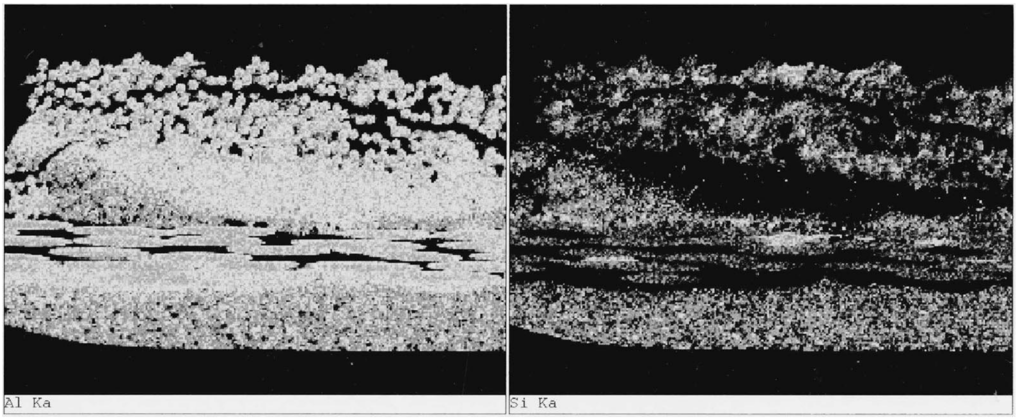

Fig. 3. Elemental map for Al and Si from Fig. 2.

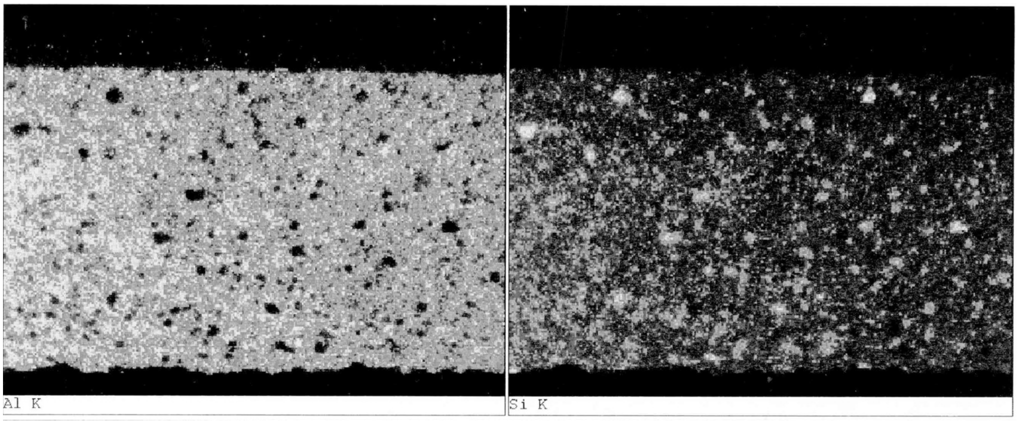

Fig. 4. Elemental map for Al and Si of monolithic deposition using Sumitomo AES21 alumina (mag.×200).

was repeated on a Imsil A8/AES 21 monolithic deposit. The alumina to silica ratio was 3.6:2. An alumina rich deposit is not detrimental to final matrix properties at high temperatures, so work was continued with Imsil A8 and Elkem microsilica in tandem.

3.2. *Fibre-ageing*

Experiments have been conducted where fibre, de-sized initially by heat treating at 600°C, are 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. X-ray diffractometry (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. 5(a) and (b)]. This would cause a decrease in strength and modulus.

Table 2
Surfactant compositions with aspartic and glutamic acids

Surfactant	Surfactant composition (main constituent ethanol)
A	0.5 M tartaric acid, 1.5 M dibutylamine, 0.5 M aspartic acid (21 vol% water)
B	0.5 M tartaric acid, 1.5 M dibutylamine, 0.5 M glutamic acid (21 vol% water)
C	0.5 M tartaric acid, 2 M dibutylamine, 0.5 M aspartic acid (21 vol% water)
D	0.5 M tartaric acid, 2 M dibutylamine, 0.5 M glutamic acid (21 vol% water)

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°C 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.

3.3. *Mullite formation and sintering*

XRD was used to determine the amount of mullite present in the sintered powder compacts. Starting compositions and heat treatment schedules are given in Table 3.

Changing the type of silica used (Elkem microsilica or Imsil A8) causes no systematic variation in the amount of mullite present after sintering when seeding with the relatively coarse KCM 73 mullite (see Fig. 6). This figure also shows that the maximum amounts of mullite are present in the most heavily seeded compacts sintered at either 1400 or 1600°C. The efficacy of the seeding is more easily quantified when the contribution to the final total amount of mullite from the seeding is subtracted (see Fig. 7). Fig. 8 shows that dramatically better results can be achieved when seeding with the much finer F1

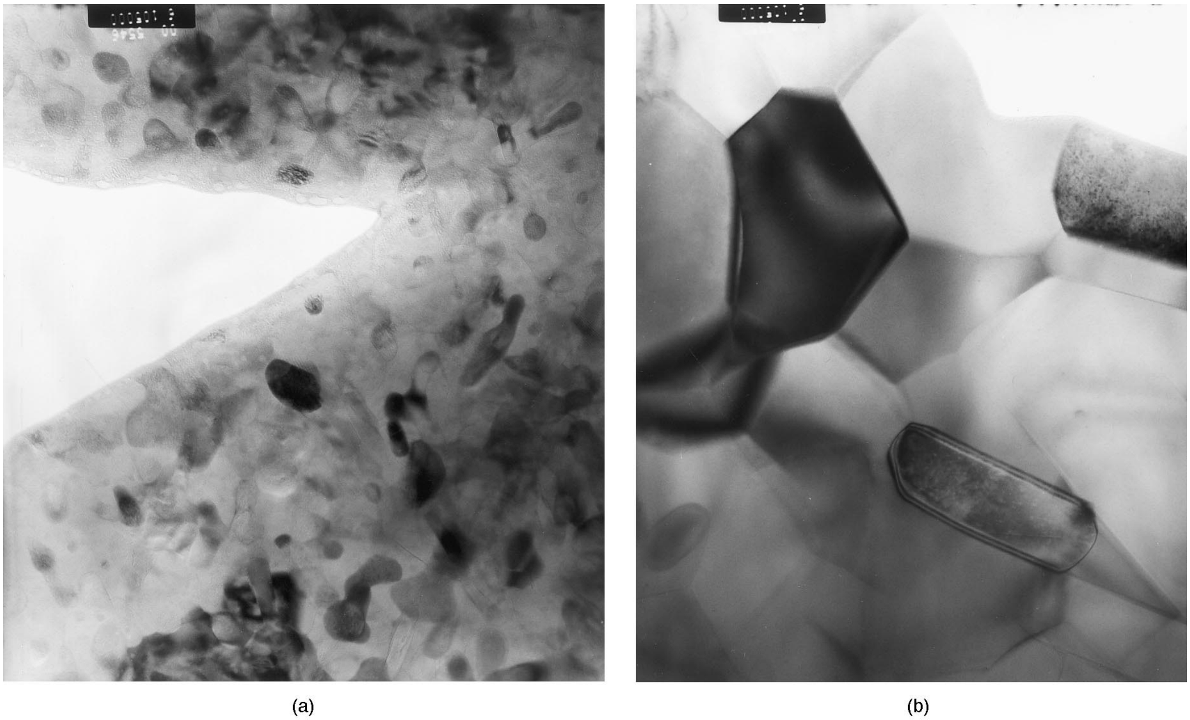
(a) (b)

Fig. 5. TEM micrograph of (a) as-received and (b) aged Nextel 720 fibres (mag.×105,000).

Table 3
Powder compact compositions[a]

Composition molar ratio Al_2O_3:SiO_2:mullite	Alumina type	Silica type	Mullite type
All powder combinations at 3:2:1, 3:2:0.5. 3:2:0.25 and 3:2 (no mullite)	AES 21	Imsil A8	KCM mullite 73
	AES 21	Elkem microsilica	KCM mullite 73
	AES 21	Imsil A8	F1 mullite

[a] All compositions were sintered for 2 h at both 1400 and 1600°C.

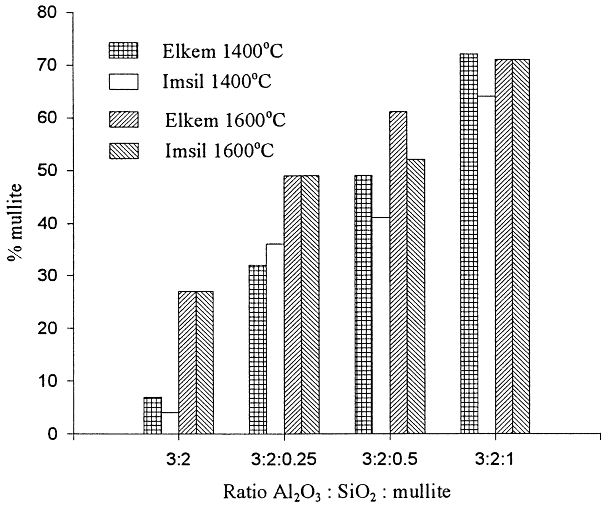

Fig. 6. Effect of different silica powders on total amounts of mullite formed in compacts seeded with KCM mullite 73.

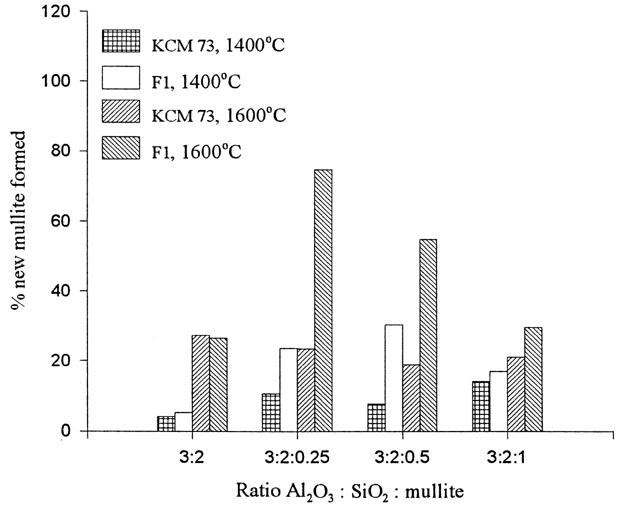

Fig. 7. Effect of mullite seeding powder on amount of new mullite formed.

powder. Complete conversion to mullite is achieved when sintering a compact with alumina:silica:mullite ratio of 3:2:0.25. Unseeded compacts sintered at 1600°C for 2 h show significant conversion to mullite. The presence of large amounts of mullite (3:2:0.5 and 3:2:1 compositions) before sintering, actually appear to inhibit mullite conversion on sintering. A large volume of this third phase might reduce the amount of diffusion between the silica and the alumina. The fine F1 mullite was more effective than the KCM mullite 73 in promoting mullite formation, probably due to its smaller particle size. Even with seeding, conversion to mullite is more efficient at the higher sintering temperature of 1600°C.

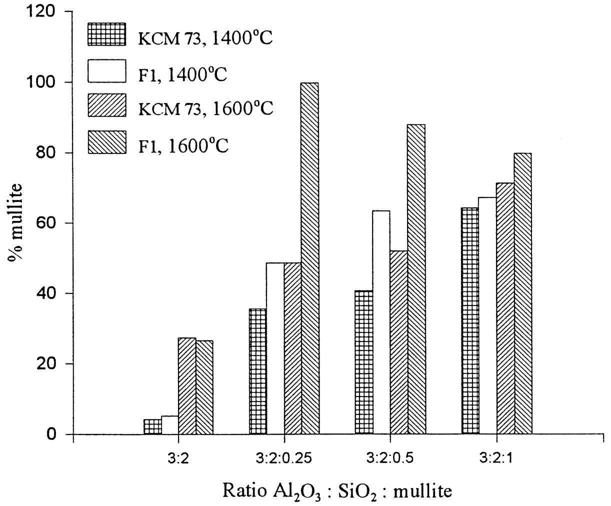

Fig. 8. Amounts of mullite present in seeded compacts after sintering.

4. Conclusions

Electrophoretic deposition is a versatile technique for ceramic composite processing. The suspension preparation route is simple and deposition rates are extremely rapid. Successful infiltration of a non-conductive Nextel 720 fibre weave by electrophoretic deposition has been demonstrated. Green body microstructures are dense with low flaw concentration. The use of ultrasonics and controlled drying may further reduce the number of flaws present. The optimisation of surfactants enabled two species infiltration resulting in green bodies with minimal phase segregation.

Seeding alumina:silica compacts with intermediate amounts of fine mullite powder promotes the same degree of mullite formation at 1400°C as is achieved in pure alumina:silica compacts sintered at 1600°C.

Production of high quality Nextel 720/mullite composition matrix green bodies which can be consolidated to form mullite-mullite composites is possible using this processing technique.

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