

PROCESSING OF NEXTEL 720/MULLITE COMPOSITION COMPOSITE USING ELECTROPHORETIC DEPOSITION

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SUMMARY: A technique for electrophoretic deposition (EPD) of alumina, silica and alumina/silica mixtures has been developed [1]. These matrices have been successfully infiltrated into electrically non-conducting 2D alumina/mullite 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 and the distribution of species within samples monitored via elemental mapping in SEM. Fibres were heat treated in air at 1400°C to assess tolerance to proposed sintering temperatures. Sintering studies were carried out at 1400°C and 1600°C on powder compacts containing alumina and silica in the mullite ratio. Compacts were seeded with mullite with the aim of reducing the temperature required for mullite formation. Infiltrated weaves were assembled with a high powder concentration aqueous suspension to form a composite block which were densified without the application of pressure at 1400°C.

KEYWORDS: electrophoresis, mullite, ceramic-matrix-composite, CMC, oxide fibre, oxide matrix, processing, sintering

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 [2]. Newly developed Nextel 720 oxide fibres provide a system capable of sustaining 1200°C at a significantly lower cost [3]. 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. Along with the need to meet performance targets, cost is one of the principal drivers for CMC development and obstacles to their application. Reduction of the complexity and duration of the production process, while maintaining material quality, would have a significant impact on the material cost. Successful densification of a fibre reinforced composite material assembled via a powder route at moderate sintering temperatures, could be

significantly cheaper than chemical vapour infiltrated (CVI) or hot-pressed materials. 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. A homogenous green body is essential if pressureless sintering is to be effective.

Materials

Nextel 720 fibres are processed via a sol-gel route. This results in a structure composed of crystalline α -alumina and mullite. The fibres are 12 μ m in diameter and have a tensile modulus of 260MPa and a tensile strength of 2100MPa. The thermal shock resistance of mullite is superior to that of alumina. Nextel 720 has acceptable mechanical properties up to 1200°C and will survive brief exposure at 1300°C [4]. The current work focuses on the green processing of a mullite fibre/mullite composition matrix composite, the transformation of a matrix consisting of separate silica and alumina powders to mullite and the densification of a composite using the conditions selected as most favourable from the sintering and seeding trials. Fibres and matrix are thus thermomechanically matched. Full transformation of the silica/mullite mix might be expected at 1600°C but as composite systems designed for operation at 1200°C should perform adequately with an alumina/aluminosilicate matrix (excess silica is detrimental to matrix properties and might react with fibres), the higher processing temperature needed for complete mullite transformation can be avoided.

Electrophoresis

Processing routes traditionally employed in the manufacture of ceramic matrix composites each have associated drawbacks. Chemical vapour infiltration is expensive due to the initial capital cost of the equipment and time associated with the repeated re-infiltration steps required to achieve adequate density. Slurry infiltration followed by hot-pressing is suitable only for the production of simple shapes and the high temperature step causes fibre property degradation. Densification of a slurry processed CMC without the application of pressure would lead to a cheaper, more versatile material and may be feasible if the green form is sufficiently dense, homogeneous and pore free [5]. Electrophoretic deposition, where charged ceramic particles in a suspension are induced to move towards and deposit on a fibre preform by the application of an electric field, has the potential to produce such green bodies. Non-conductive fibres, such as Nextel 720 must be placed in front of the deposition electrode and then the deposit forms around the fibres [1].

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:

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

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

A suspension for effective 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 and 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 charge and sign of the particles should be tailored to allow deposition at the electrode where gas evolution is avoided. Careful cell set up and field regulation, along with suspension optimisation should lead to the production of a dense, uniform deposit.

EXPERIMENTAL PROCEDURE

Surfactants

Surfactants were added to ethanol suspensions of alumina and silica to modify particle mobility. The behaviour of alumina suspensions with various surfactants containing a carboxylic acid and an amine was characterised [1]. The highest electrophoretic mobility, and by implication, stability, of a 5vol% alumina suspension was obtained by adding a surfactant composed of 0.5M tartaric acid/1.5M dibutylamine (16vol% water).

Deposition and Infiltration

Depositions of alumina (Alcan Baco RA207LS or Sumitomo AES 21) and silica (Elkem Microsilica) from single and then dual species suspensions were made initially onto a flat plate. The relative deposition rates (by mass) were quantified from the single species deposits. Mixed deposits were analysed for aluminium:silicon ratio by inductively coupled plasma atomic emission spectrometry. A 3:2 alumina to silica ratio is required in the final product for stoichiometric mullite. Elemental mapping by EDX in SEM was used to assess the extent of any segregation.

In an analogous manner, single species suspensions were used to infiltrate Nextel 720 weaves before deposition from mixed suspensions was attempted. Infiltrated weaves were epoxy mounted, cross sectioned and examined for the extent and quality of infiltration. Weaves infiltrated with two species were analysed by elemental mapping in SEM for aggregates. Mullite seeding of the composite matrix was attempted by infiltrating weaves from a three component suspension. The ratio of deposited powders from the 3 component suspension was analysed by XRD.

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 62.5V/cm, applied for up to 7 minutes in constant voltage mode.

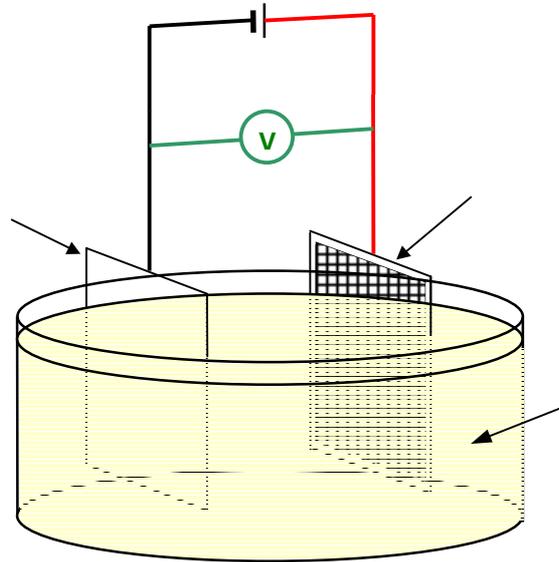


Fig. 1: Electrophoresis set up for composite manufacture

Fibre ageing

In order to provide a cost effective manufacturing route, it is intended that the oxide-oxide composite green bodies produced should be densified by pressureless or gas pressure sintering. This requires higher temperatures than hot-pressing, and thus the success of the method is critically dependant on the ability of the fibre to withstand sintering at temperatures up to 1400°C and to go on to perform adequately in sintering. Hence, one of the first investigative steps in developing the manufacturing process was to age the Nextel 720 fibre weaves in air at 1400°C for 24hrs.

Sintering

Uniaxially pressed mixed powder disks were sintered at 1400 and 1600°C. Mullite was added to a selection of the compacts in order to assess the effectiveness of seeding in mullite formation. Two different mullite powders were used; milled KCM sintered mullite 73 (particle size 0.00 – 0.08mm) and a 1µm mullite [7]. 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. The monolith sintering study indicated that milled KCM mullite was more effective and so seeding of infiltration into weaves was carried out with milled KCM sintered mullite 73. A high powder volume content (43vol%) aqueous suspension was used to layer infiltrated weaves together into blocks which were sintered for 4hrs at 1400°C.

Experience of Sacks et al. [8] 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 2wt% of an extremely fine mullite powder (median particle size ~0.15µm) mullite powder results in almost complete conversion to mullite at 1400°C.

RESULTS AND DISCUSSION

Electrophoresis

Rates of deposition

The rates of deposition of the individual species were investigated with monolithic depositions. The deposition rates of dry matter were calculated as 0.04g.min⁻¹cm⁻² for Alcan Baco RA207LS alumina and 0.06 g.min⁻¹cm⁻² for the Elkem micro silica. Deposition of both alumina and silica was rapid and thick deposits formed in less than 2 minutes.

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 (2.16v% Alcan alumina, 1.36v% Elkem micosilica). The green body formed had a mean molar ratio of 3.1:2 alumina to Elkem micosilica. Two further depositions were carried out from a fresh suspension, replacing Alcan with Sumitomo alumina (2.25v% AES 21 alumina, 1.46v% 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.

Table 1 Alumina:silica molar ratios achieved on deposition with alumina and Elkem micosilica.

<i>Suspension</i>	<i>Deposition sequence</i>	<i>Molar ratio Al₂O₃: SiO₂</i>
2.13v% Alcan alumina, 1.35v% silica	First	3.12 : 2
2.13v% Alcan alumina, 1.35v% silica	First	3.13 : 2
2.22v% Sumitomo alumina, 1.46v% silica	First	3.37 : 2
2.22v% Sumitomo alumina, 1.46v% silica	First	3.47 : 2
2.22v% Sumitomo alumina, 1.46v% silica	Second	3.42 : 2
2.22v% Sumitomo alumina, 1.46v% silica	Second	3.34 : 2

Further suspension optimisation was unnecessary because the molar ratio of alumina to silica was considered acceptably close to 3:2, and errs on the alumina rich side, which is preferable for good high temperature properties. 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 AES 21 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 7m²g⁻¹ and AES 21 is 3.5-4m²g⁻¹) but may be attributed to its greater density and size.

Infiltration

Alumina was infiltrated into a Nextel 720 weave producing a homogenous distribution of ceramic powder around the fibres with occasional voids (Fig. 2 (a)). Full infiltration was

achieved in 2 minutes. 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.

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). Some drying cracks were observed in the weave and infiltration was extensive but not complete (see Fig. 2 (b)). The large crack in the centre of the sample has been attributed to the epoxy curing stage. The elemental maps show some segregation of alumina and silica and silica aggregates of the order of 10-20 μ m had formed, Fig. 3. Silica aggregates were also seen in the monolithic deposit.

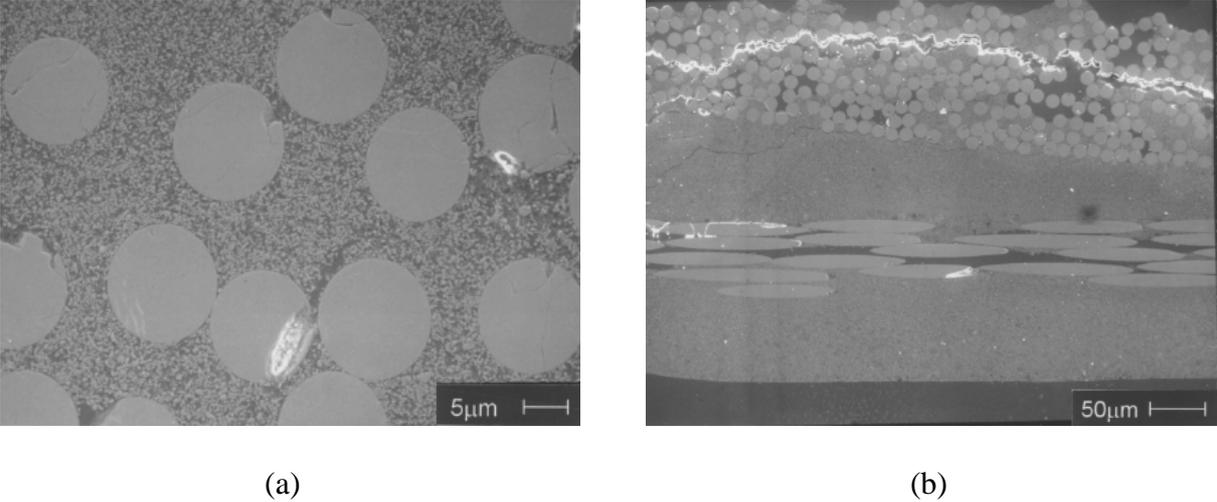


Fig 2: (a) SEM micrograph of Al alumina infiltration, (b) SEM micrograph Al alumina and silica co-infiltrated

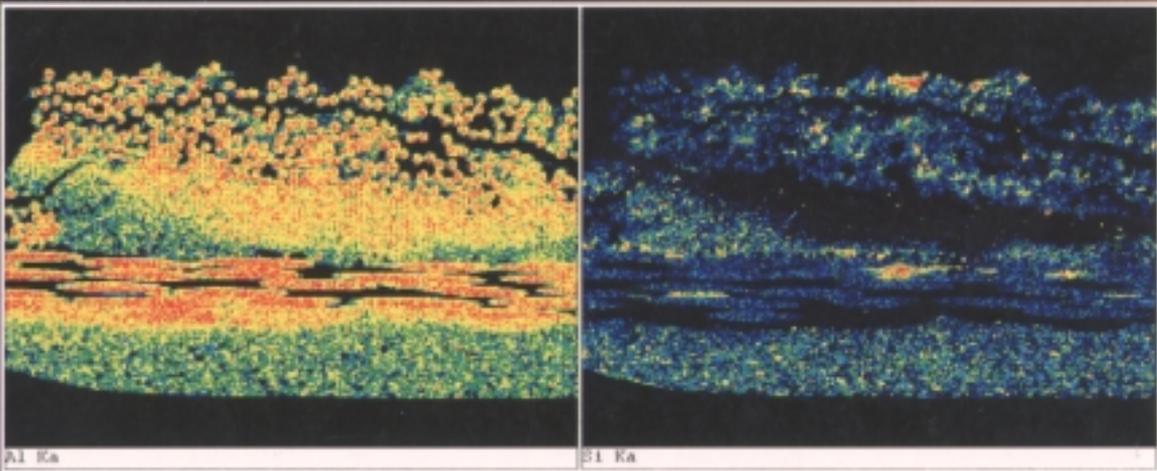


Fig 3: Elemental map for Al and Si from Fig. 2(b)

Alternative surfactants, using different and mixed carboxylic acids were assessed but had little or no effect on the formation of silica aggregates. Two new silica powders were tested,

Acematt HK400 and Imsil A8. The former was difficult to handle and formed low density deposits and larger aggregates than the Elkem silica. Imsil A8, however, produced monolithic deposits of similar quality to the Elkem powder containing smaller regions of silica. Elemental analysis by ICPAES 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.

Fibre Ageing

Fibres were de-sized initially by heating to 600°C and then aged by holding at a temperature of 1400°C for 24hrs. The appearance and handling characteristics of aged fibres was little different to those in the as received state. XRD showed little change in composition, however TEM examination revealed a 15 fold increase in grain size [1]. Other workers have found a 20% fall in tensile strength to 1500 MPa when fibres are held at 1200°C [3] 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 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.

Mullite Formation and Sintering

Molar ratios of alumina:silica:mullite of 3:2:1, 3:2:0.5, 3:2:0.25 and 3:2 (no mullite) were chosen to investigate the effect of mullite seeding on mixed powder compacts without fibres. All possible combinations of AES 21 alumina with either of the two silica powders (Imsil A8 and Elkem microsilica) and either of the mullites (KCM mullite 73, milled to give a finer particle size, and 1µm mullite) were sintered for two hours at 1400°C and 1600°C. This initial investigation indicated that the type of silica powder used had no influence on the amount of mullite formed (as quantified by XRD) and that when sintering compacts at 1600°C, 25-30% mullite was produced in both seeded and unseeded compacts. For a 2 hour hold, seeding appeared to increase the amount of mullite present when sintering at 1400°C. Results were more consistent when using KCM 73 mullite. As there was some uncertainty about the exact composition of the 1µm mullite, the second set of sintering tests at lower temperatures more realistic for composite densification were carried out only with KCM mullite. Experiments are detailed in Table 2 and the results in Table 3.

Table 2: Compositions and sintering conditions for seeding tests

<i>Molar ratio of alumina to silica to mullite</i>	<i>Alumina</i>	<i>Silica</i>	<i>Mullite</i>	<i>Time at 1300°C (hours)</i>	<i>Time at 1400°C (hours)</i>
3:2:1	AES21	Imsil A8	Milled KCM mullite 73	4	2 and 4
3:2:0.5, 3:2:0.25 and	AES21	Imsil A8	Milled KCM mullite 73	4	2 and 4
3:2 (no mullite).	AES21	Imsil A8	Milled KCM mullite 73	4	2 and 4

Table 3: Mullite formation from sintering of AES alumina/ Imsil A8 silica/ milled KCM mullite 73

<i>Molar ratio alumina:silica:mullite</i>	<i>% mullite formed after sintering at 1300°C for 4 hours</i>	<i>% mullite formed after sintering at 1400°C for 2 hours</i>	<i>% mullite formed after sintering at 1400°C for 4 hours</i>
3:2:1	13	26	28
3:2:0.5	9	24	29
3:2:0.25	4	25	28
3:2 alumina:silica	none	18	31

Comparing each column of results in Table 3 to that for and unseeded compact sintered under the same conditions shows that seeding is most effective at 1400°C for a two hour soak at temperature. A 4 hour hold at 1400°C is more effective in producing mullite, but it appears that as the highest mullite figure is seen for the unseeded compact, that this is attributable to the length of hold.

Composite manufacture and sintering

An aqueous suspension containing 42vol% of powders (AES21 alumina, Imsil A8 silica and milled KCM mullite) was produced by mixing and homogenisation using an ultrasonic disrupter probe. De-sized 2D Nextel 720 fibres were used in 8 harness, satin weave form. The warp and fill count is 11 yarns/mm. The weaves were infiltrated by EPD under the conditions listed in the experimental section and immediately sandwiched together with the thick suspension while wet. A block was constructed using 12 layers of fibres. The block was allowed to dry and sintered for 4 hours at 1400°C.

The block was infiltrated with a low viscosity resin under vacuum, sectioned and examined in SEM. Initial indications show that the large cracks present in the layers of monolith between fibre weaves (Fig. 4) were caused by shrinkage on drying and that sintering was achieved without causing further flaws. Electrophoretic infiltration into the weave structure is dense and apparently complete. No remnant of the interface between the weaves and thick suspension is seen. The fibres appear unaffected by sintering.

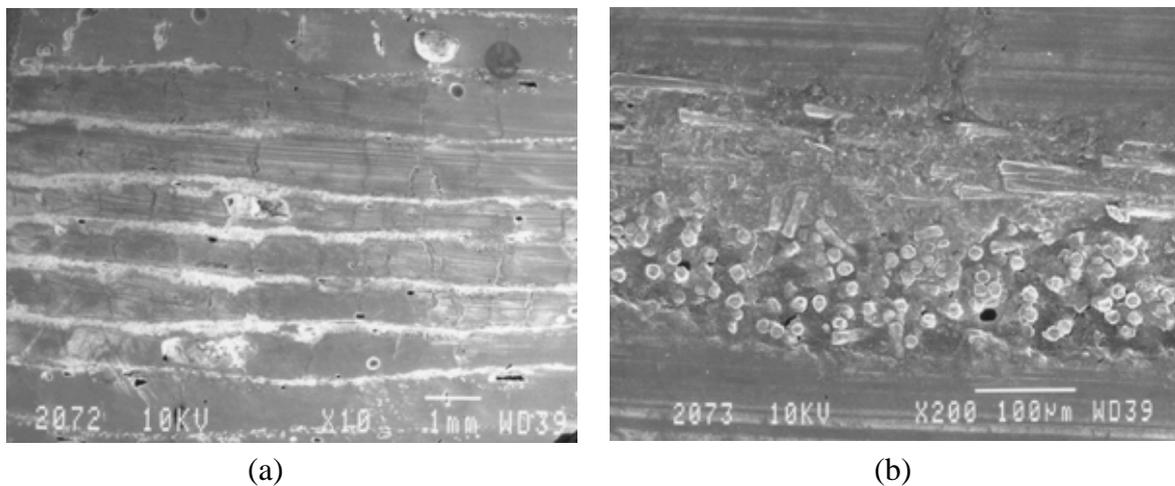


Fig 4: Sintered microstructure of composite block (a) at low magnification showing drying cracks between weaves and (b) detail showing the dense infiltration of powder within a fibre weave.

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.

Conversion of alumina and silica to mullite at the temperatures demanded by the Nextel 720 fibres is not complete. Seeding of compacts with crystalline mullite powder encourages conversion at 1400°C when the sintering time is 2hrs, but for a sintering hold of 4hrs, the seeding has little effect.

Production of Nextel 720/mullite composition matrix composite green bodies which can be consolidated to form mullite-mullite composites is possible using a combination of EPD and slurry processing is possible but requires development. Densification by sintering without pressure appears feasible.

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REFERENCES

1. Westby, W.S., Kooner, S., Farries, P.M., Boothe, P., and Shatwell R.A., 'Processing of Nextel 720/mullite composition composite using electrophoretic deposition', *Journal of Materials Science*, in press, 1999.
2. Lundberg, R. and Eckerbom, L., 'Design and Processing of All-Oxide Composites', *Proceedings of the Second International Conference on High-Temperature Ceramic Matrix Composites, Santa Barbara, CA, USA, August 21-24, 1995, Ceramic Transactions, Vol. 58*, Evans, A.G. and Naslain, R., Eds, pp. 95-104.
3. Manufacturers information, 3M Company, Ceramic Materials Department, St.Paul, Minnesota, USA.
4. Kerans, R. and Parthasarathy T.A., Private Communication, 1997.
5. Kooner, S., Campaniello, J.J., Pickering, S. and Bullock, E., 'Fibre reinforced ceramic matrix composite fabrication by electrophoretic infiltration' *Proceedings of the Second International Conference on High-Temperature Ceramic Matrix Composites, Santa Barbara, CA, USA, August 21-24, 1995, Ceramic Transactions, Vol. 58*, Evans, A.G. and Naslain, R., Eds,p155.
6. Brinker, C.J. and Scherer, G.W., *Sol-Gel Science*, Academic Press, 1990

7. I. Rouse, Pi-Kem, Shropshire, *Private Communication*, 1998.
8. M.D. Sacks, Y-J. Lin, G.W. Scheiffele, K. Wang and N. Bozkurt, 'Effect of seeding on phase development, densification behaviour and the microstructural evolution in mullite fabricated from microcomposite particles', *J. Am. Ceram. Soc.*, **78**[11] (1995) 2897-2906.