

# Electrophoretic Deposition Infiltration of 2-D Woven SiC Fibre Mats with Mixed Sols of Mullite Composition

A. R. Boccaccini,<sup>\*a</sup> I. MacLaren,<sup>b</sup> M. H. Lewis<sup>c</sup> & C. B. Ponton<sup>a,b</sup>

<sup>a</sup>School of Metallurgy and Materials, The University of Birmingham, Birmingham, B15 2TT, UK

<sup>b</sup>IRC in Materials for High Performance Applications, The University of Birmingham, Birmingham, B15 2TT, UK

<sup>c</sup>Department of Physics, University of Warwick, Coventry, CV4 7AL, UK

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## Abstract

*Electrophoretic deposition (EPD) has been used to infiltrate a dual-component mixed sol of mullite composition into woven, electrically conducting SiC (Nicalon) fibre preforms. Both silica and alumina precursors had a near-equiaxed particle shape and their controlled colloidal mixing at an optimised pH (3.1) has led to their extensive heterocoagulation on a nanometre scale. The mechanisms of particle migration in the EPD cell are not fully clear at this stage. It is suggested that both sol species migrate simultaneously as a 'composite' sol particle to the fibre mat serving as one electrode in the cell. Owing to the small particle size of the silica and alumina used, both components were able to infiltrate the spaces within the fibre tows. Good particle packing and a high solids-loading were achieved, producing a firm matrix deposit which adhered to the fibres. The maintenance of the stoichiometric mullite composition in the deposited material was confirmed by XRD analysis of the deposited material heat-treated at 1350°C for 5 h. The high-quality infiltrated fibre mats serve as preforms for the fabrication of mullite matrix composites. © 1997 Elsevier Science Limited.*

## 1 Introduction

The development of ceramic fibre reinforced ceramic matrix composites is a promising means of achieving structural materials combining high-

temperature strength with improved fracture toughness and damage tolerance.<sup>1</sup> The incorporation of reinforcing fibres in the ceramic matrix provides the ceramic-ceramic composite body with a 'pseudo-ductility' not possessed by monolithic ceramics. Potential applications of these materials are in gas turbines, aero-engines and energy-conversion systems, where they may have significant advantages over the metal alloys employed currently.<sup>2–4</sup>

Considerable research effort is being expended on the optimisation of ceramic matrix composite material systems, with particular emphasis being placed on the establishment of reliable and cost-effective fabrication procedures. In this context, while the initial efforts were in fabricating unidirectional composites, they now seem to be shifting towards the more isotropic, woven-fibre reinforced materials,<sup>5</sup> including non-oxide/non-oxide systems (e.g. SiC/SiC<sup>5–7</sup>), oxide fibre/oxide matrix systems (e.g. alumina/alumina<sup>8</sup> and mullite/mullite<sup>9</sup>) and non-oxide fibre/oxide matrix systems (e.g. SiC fibre/mullite matrix<sup>9–11</sup>). Ceramic composites incorporating 2- or 3-dimensional fibre reinforcement are particularly prone to exhibiting uncontrolled microstructures and residual porosity. This is because it is extremely difficult to achieve complete infiltration of the matrix material into the fibre tows (where the intra-tow openings are of the order of  $\leq 100$  nm). Although a number of processing methods have been considered in the last few years, including chemical vapour infiltration, polymer impregnation pyrolysis, melt oxidation, melt infiltration, sol-gel infiltration and slurry infiltration (for a review of such routes, see<sup>12</sup>), there is still a need to improve/optimize the different approaches.

\*Present address: Fachgebiet Werkstofftechnik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany.

A novel, simple and inexpensive method for achieving complete infiltration of tightly woven fibre preforms has been developed recently.<sup>13,14</sup> It is based on the electrophoretic deposition (EPD) of colloidal ceramic sols into the fibre preforms. Using nanoscale ceramic particles in a non-agglomerated form (particle size  $\sim 5\text{--}50\text{ nm}$ ), and exploiting their net surface electrostatic charge characteristics while in colloidal suspension, provides an appropriate means of effectively infiltrating the densely packed fibre bundles.

An excellent article dealing with the principles of EPD and containing a complete review on the application of EPD in ceramics has been published recently.<sup>15</sup> Briefly, the EPD process relies on the presence of small-charged powder particles within a colloidal suspension which, on the application of an electric field, will migrate toward and deposit on an electrode, a phenomenon known from the beginning of the last century.<sup>16</sup> Movement of the particles occurs because the particle surfaces are charged with respect to the suspending medium. The electrostatic surface charge field decays to zero over a certain distance away from the particle into the suspending liquid. When this distance is large compared with the radius of the particle, the particle will move with respect to the surrounding liquid when subject to an applied external electric field and deposit on either the anode or the cathode, depending on its polarity. A schematic diagram of the basic EPD cell is shown in Fig. 1. If the deposition electrode is replaced by a conducting fibre preform, the suspended particles will be attracted into the fibre preform and deposited within it, resulting in complete infiltration. The movement of ceramic sol

particles in an aqueous suspension within an electric field is governed mainly by factors such as the field strength, the pH of the solution and the ionic strength of the solution.<sup>14,15,17</sup>

The feasibility of the process to infiltrate two-dimensional woven fibre preforms has been demonstrated for single component sols. For example, silica<sup>14</sup> and boehmite<sup>8</sup> sols were used for the fabrication of silica matrix and alumina matrix composites, respectively. However, its applicability to two-component mixed sols has been explored only partially.<sup>11,18</sup> This paper reports on the optimization of the technique for infiltrating woven fibre preforms using two-component mixed sols with the mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) composition. The investigation includes the selection of novel yet suitable silica and alumina precursors and the determination of the best conditions for the colloidal processing of these precursors sols and their subsequent electrophoretic infiltration into, and deposition onto, ceramic fibre preforms. In a separate study, the densification and mullitisation behaviour of the matrix material obtained from the same precursors has been investigated.<sup>19</sup> The results of these investigations advance the understanding of how to fabricate 2-D woven-fibre reinforced mullite matrix composites successfully which, despite their potential for high-performance applications owing to the excellent high-temperature mechanical properties of mullite,<sup>20,21</sup> have received only limited consideration in the literature to date.<sup>9-11,22</sup>

## 2 Experimental procedure

A commercially available silicon carbide plain woven fibre preform (Nicalon 607C, Nippon Carbon Co., Japan) was used in this study. These fibre preforms have been shown to be suitable for ceramic matrix reinforcement.<sup>10,13</sup> The fibres have an average diameter of approximately  $15\ \mu\text{m}$ . They also possess a residual carbon surface layer ( $\sim 100\text{ nm}$  thick) as a consequence of the manufacturing process, which endows the fibres with sufficient electrical conductivity to be used successfully as the deposition electrode during EPD. The fibre architecture considered was a 2-D plain-woven multifilament fibre because plain weave is the tightest of the weaves available, making it the most difficult to infiltrate and, hence, the ultimate benchmark for demonstrating the potential of the EPD technique.

The selection of the starting silica and alumina precursors was made on the basis of a number of requirements. First, no NaOH-stabilized silica

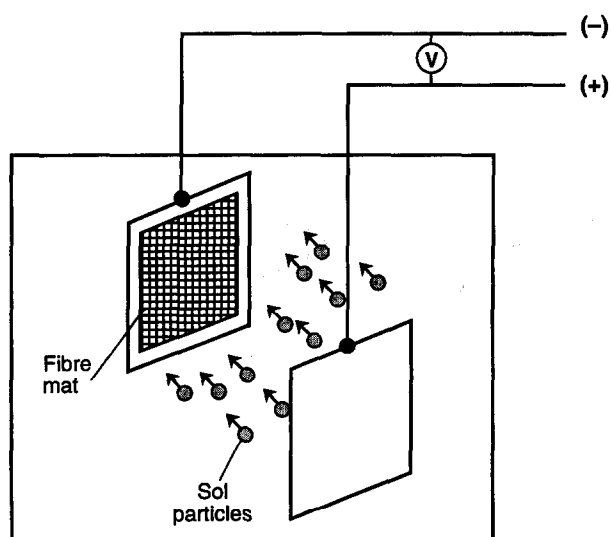


Fig. 1. Schematic diagram of an electrophoretic deposition cell using a conductive fibre mat as the negative electrode.

sols were selected, as they are prone to crystallisation and cristobalite formation at relatively low temperatures, which would prevent full densification of the mullite precursor matrix during the high-temperature consolidation process.<sup>23</sup> Second, the easy availability, low cost and environmental safety of the materials were also taken into consideration when selecting the precursors. On the basis of these primary criteria, organometallic compounds were not considered. Furthermore, the shape and size of the colloidal particles of the two species were also taken into account, since they determine both the scale and quality of mixing of the two sols and, hence, the stoichiometry of the deposited material. Previously, spherical silica particles with a broad particle size distribution (10–100 nm, average particle size of 40 nm) and a boehmite ( $\gamma$ -AlOOH) sol (as a precursor for alumina) having an average particle size of 50 nm with a fibrillar particle morphology, were used.<sup>11</sup> Although this combination of precursors led to good infiltration of the fibre preforms in terms of a high solids-loading, the stoichiometry of the deposited material was not maintained as that of mullite throughout the preform, resulting in the presence of a glassy phase upon heat-treatment at 1300°C, as detected by X-ray diffraction analysis.<sup>11</sup>

In this present study, both the silica and alumina particles were required to be of equiaxed morphology. The appropriate (commercially available) precursors were therefore:

- (1) A fumed silica/alumina liquid dispersion containing 1 wt%  $\delta$ -alumina (Aerosil K342, Degussa Ltd, UK). The mean particle size is 30 nm and the pH of the as-received suspension is in the range 4–6.<sup>24</sup>
- (2) Fumed alumina ( $\delta$ -alumina) (Aluminium Oxide C, Degussa Ltd, UK). This is a highly dispersible alumina powder with average particle size of 13 nm. The pH in water ranges from 4.5 to 5.5.<sup>25</sup>

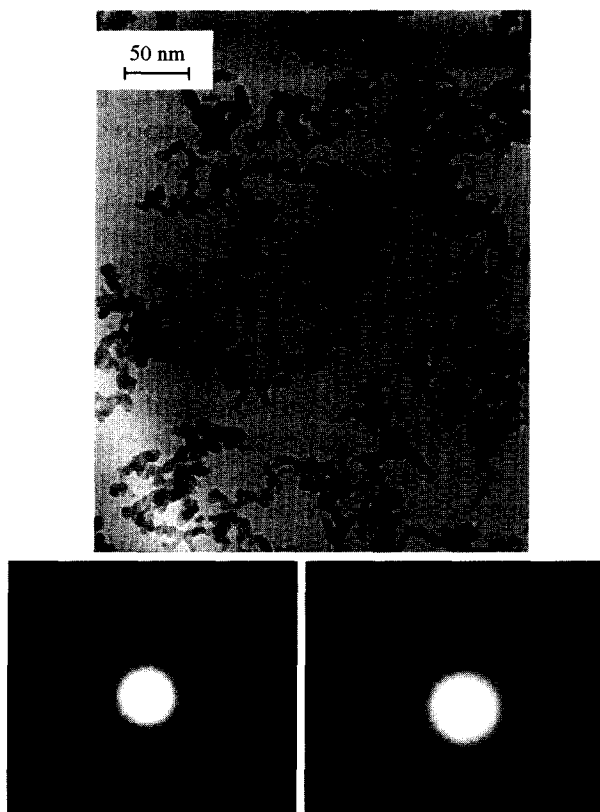
The precursors were mixed in proportion such that the resulting ceramic after sintering would be stoichiometric mullite, i.e. 72 wt% alumina–28 wt% silica. After adding the fumed alumina gradually to the silica/alumina liquid dispersion, the pH of the sol was adjusted by adding 0.1 M HCl dropwise, while stirring. At a pH of 3.1, a clear, stable mixed sol was obtained, appropriate for the EPD studies. The relative spatial arrangement of the alumina and silica particles within the sol and the degree of mixing were investigated by transmission electron microscopy (TEM) as they are critical factors, not

only for achieving a high degree of infiltration during EPD but also for obtaining dense mullite at relatively low temperatures ( $\sim$ 1300°C) during the consolidation of the ceramic composites.<sup>19</sup> The samples for TEM observations were fabricated in the following manner. Thin carbon films mounted on copper grids were prepared and dipped into the mixed sol in order to pick up some of the particles. These were then placed on absorbent paper to dry. These specimens were examined in a Philips CM20 TEM operating at 200 kV using bright field imaging (BFI) and selected area diffraction (SAD).

For the EPD experiments, 50 mm  $\times$  50 mm squares were cut from the as-received silicon carbide fibre preform. They were placed in the colloidal suspension, and then vacuum degassed before being infiltrated by EPD. During EPD the fibre mats served as the negative 'deposition' electrode and a stainless steel plate as the positive electrode (see Fig. 1). A standard d.c. power supply was used for providing the electric field. A d.c. voltage of 4 V was applied to the electrodes, which were separated 3 cm. The deposition time was varied to find the optimum time for the complete infiltration of the sol into the intra-tow regions, and for obtaining the desired thickness of the deposited surface layer on the mat. The infiltrated fibre fabrics were dried slowly in a humid atmosphere ( $\sim$ 80% humidity). The dried impregnated fibre mats were polished to a 1  $\mu$ m finish for optical and scanning electron microscopy (SEM) examination and SEM energy dispersive X-ray analysis (EDX). Some dried impregnated fibre mats were heat-treated for 5 h at a temperature of 1350°C. Matrix material from the inter/intra tow regions was removed, powdered and analysed using X-ray diffractometry (XRD). The purpose of this analysis was to confirm that the electrophoretically deposited material had maintained the mullite composition of the original sol, as reported below.

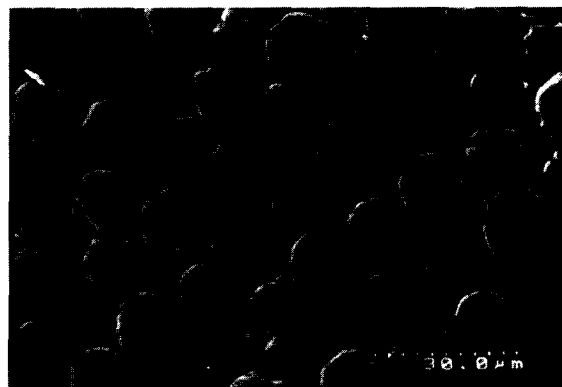
### 3 Results and Discussion

Figure 2 shows a TEM bright field image (BFI) of the ultrafine alumina and silica particles in the mixed sol. These particles have a slightly irregular morphology but are usually close to equiaxed. There is very little difference in morphology and size between the alumina and silica particles but they can be distinguished by use of selected area diffraction (SAD) since the  $\delta$ -alumina particles are crystalline whilst the silica particles were amorphous. Examples of SAD patterns taken from



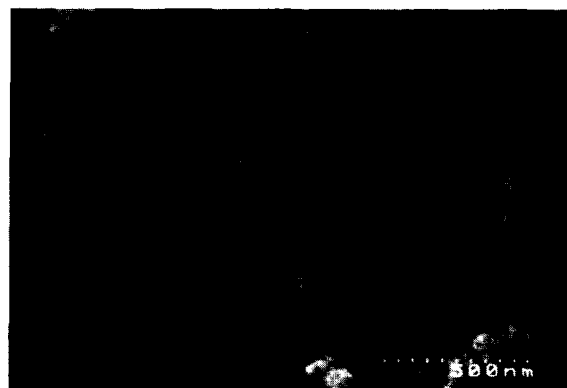
**Fig. 2.** TEM bright field imaging (BFI) micrograph of the mixed alumina/silica sol at pH=3.1, showing the intimate nanometre scale mixture of near-equiaxed silica and  $\delta$ -alumina particles. The inserts represent selected area diffraction images of a  $\delta$ -alumina particle showing its crystalline nature (left) and of a silica particle showing its amorphous nature (right).

amorphous silica particles and  $\delta$ -alumina particles are shown as inserts in Fig. 2. Moreover, the TEM BFI micrograph of the sol shows that the alumina and silica particles are mixed intimately on a sub-100 nm scale. The zeta potential versus pH curves for alumina and silica nanoparticles in colloidal suspensions, as shown in the literature,<sup>26</sup> provide the explanation for this particle arrangement. At a pH between 2 and 9, both species are oppositely charged; therefore, a strong electrostatic attraction exists between the positively charged alumina particles and the negatively charged silica particles. In this pH range, the mutual electrostatic attraction is expected to lead to heterocoagulation and, hence, the maximum pairing of unlike particles (AB). The optimum pH for such pairing to occur has been found to be in the range of 3 to 5.<sup>26</sup> The pH of the above mixed sol was tailored to be in this range; i.e. pH 3.1. It is envisaged that the occurrence of more AB pairings than identical particle clusters, i.e. AA and BB pairings, in the sol will help to maintain the desired mullite stoichiometry of the electrophoretically deposited material during EPD.



**Fig. 3.** SEM micrograph of an impregnated fibre mat, showing that during EPD the mullite composition mixed sol has infiltrated fully the intra-tow regions.

Figure 3 shows an SEM micrograph of an infiltrated fibre mat. It can be observed that EPD is capable of producing a high level of particle infiltration into the electrically conducting fibre tows. Using a conducting Nicalon woven fibre mat as the deposition electrode and a relatively low d.c. voltage of 4 V enhances the infiltration process by opening up the spaces in the fibre tow through the mutual repulsion of the charged fibres. Owing to the small particle size of the silica and alumina used, both components are able to infiltrate the spaces within the fibre tows. Figure 4 shows a high-resolution SEM image (Hitachi S4000 FEG SEM) of the matrix material within the fibre tows. Good particle packing and a high solids-loading were achieved, producing a firm matrix deposit which adhered to the fibres. The use of a low EPD voltage minimised the electrolyte decomposition and subsequent gas evolution, which was found to occur in previous work.<sup>14</sup> A deposition time of 1 min was found to yield complete infiltration while keeping the deposited layer thickness low enough to prevent cracking upon drying in air. Thin films (i.e. < 1  $\mu\text{m}$  thick) can



**Fig. 4.** High-resolution SEM micrograph of the EPD deposited material between the fibres within the fibre tows, showing good particle packing.

be dried in air without cracking because the tensile stresses generated on shrinkage are too low to cause the growth of cracks from microscopic flaws.<sup>27</sup> The infiltrated fibre fabrics in this study were dried slowly in a humid atmosphere ( $\sim 80\%$  humidity); as a consequence, no crack formation in the matrix between the fibres was apparent.

The most important requirement to be fulfilled by the mixed sol is that both species (i.e. the alumina and silica particles) move to the same electrode in the EPD cell. Semi-quantitative EDX spot analysis of the matrix regions between the fibre tows revealed the presence of both aluminium and silicon (as Fig. 5 shows), confirming that both sol particle species have migrated to the woven fibre mat serving as the negative electrode. The modelling of the mobility and migration behaviour of the differently charged particles in the EPD cell is the subject of current study. The fact that both species migrate to the same electrode (i.e. the cathode) can be explained, at least qualitatively, by considering the formation of 'composite' particles in the suspension at the working pH, i.e. heterocoagulated particle clusters consisting of mutually attractive discrete alumina and silica particles (see Fig. 2), which exhibit a net overall positive electrostatic surface charge, implying either a greater number of alumina sol particles per cluster or a 'core' silica sol particle surrounded by an alumina sol particle 'shell'. The TEM BFI micrograph (see Fig. 2) indicates that the former particle spatial arrangement is the more probable. If the same kind of heterocoagulated particle cluster (in terms of overall size, morphology and surface charge character-

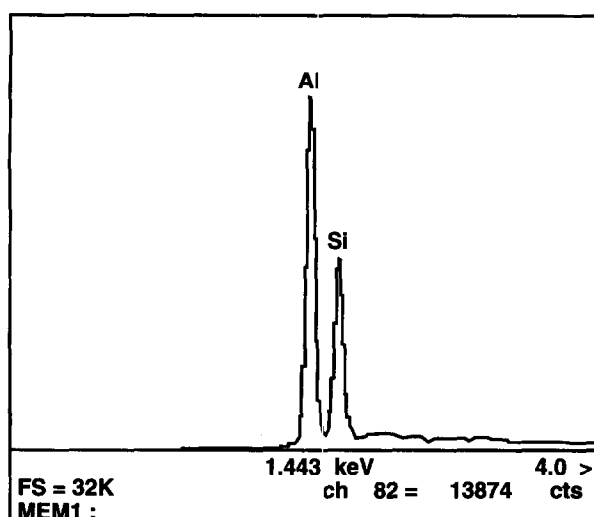


Fig. 5. EDX spot analysis of the deposited material between the fibres within the fibre tows showing the presence of aluminium and silicon and, hence, indicating that both species have migrated to the same electrode during EPD.

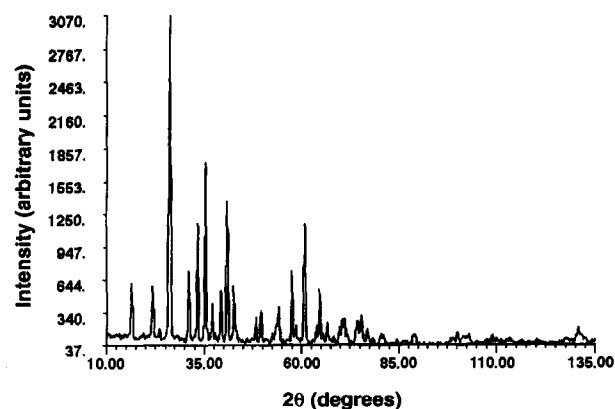


Fig. 6. Powder XRD pattern of ceramic material deposited onto a Nicalon fibre mat by EPD after heat-treating for 5 h at  $1350^{\circ}\text{C}$ . Mullite is the only crystalline phase detected.

istics) is formed throughout the suspension, which will depend on the relative shape and size of the particles, then all these 'composite' particles will have the same probability of migrating to the negative electrode at similar rates and, consequently, the original mullite stoichiometry of the colloidal mixed sol will be maintained within the deposit. The maintenance of the stoichiometric mullite composition in the deposited material was examined by subsequent XRD analysis of the deposited material heat-treated at  $1350^{\circ}\text{C}$  for 5 h. The pattern indicates that mullite was the only crystalline phase present, as shown in Fig. 6. In addition, there is no amorphous halo visible in the XRD pattern, which indicates the absence of any XRD significant quantity of a residual silicate glassy phase. In a previous study where other precursors were employed,<sup>11</sup> a significant amorphous halo was observed in the XRD pattern, evidentiating a low crystallinity of the deposited material. This result confirms that the ultrafine, near-equiaxed silica and alumina sols used in the present study provide optimised starting materials for producing mullite-composition mixed sols suitable for the EPD infiltration technique. The preparation of composite materials using the so-prepared high-quality infiltrated prepreps by stacking and hot-pressing is the focus of current work.

#### 4 Conclusions

Summarizing, it has been demonstrated that the EPD sol infiltration technique can be used to successfully infiltrate a dual-component mixed sol, such as alumina/silica of mullite composition, into woven, electrically conducting fibre preforms. The selection of both near-equiaxed silica and alumina

precursors and their controlled colloidal mixing at an optimised pH (3.1) has led to extensive heterocoagulation of sol particles on a nanometre scale, allowing both sol species to migrate simultaneously as a 'composite' sol particle to the fibre mat serving as one electrode in the EPD cell. The plain-weave architecture of the woven Nicalon fibre mats, which is the tightest fibre weave architecture, could be infiltrated fully. This implies, therefore, that EPD should infiltrate successfully other, less tightly woven, fibre preforms. Thus, the way is opened for the development of 2- or 3-dimensional reinforced oxide ceramic matrix composites with two-, or even multi-component matrices, which show superior high-temperature mechanical properties in comparison with single oxide matrices. The ability to prepare dense deposits of mullite ceramic material by the EPD technique, using commercially available and inexpensive alumina and silica sols, may also have general applicability in coating technology.

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