

# Deposition of zirconia sols on woven fibre preforms using a dip-coating technique

X. Gu<sup>a,\*</sup>, P.A. Trusty<sup>a,1</sup>, E.G. Butler<sup>a</sup>, C.B. Ponton<sup>a,b</sup>

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

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

Received 1 September 1998; received in revised form 12 July 1999; accepted 8 August 1999

---

## Abstract

The technique of depositing zirconia coatings onto woven fibre mats has been investigated in detail. The application of a coating to the fibre is essentially one of the easiest methods of providing a fibre–matrix interface with desired properties. Such coatings can act as reaction barriers or as fibre–matrix debond interfaces. This particular coating method, which is the dip-coating of fibre tows in zirconia sols, does not require sophisticated apparatus and, therefore, has great potential as a standard coating technique for use with woven fibre systems. In this work, an “in-house” produced zirconia sol, synthesised using hydrothermal processing, has been found to be the most successful coating material. Both alumina and alumina-silica woven fibre mats were used as the substrate materials. It has been shown that the zirconia sol employed can be deposited successfully in a single coating step, as a thin (1–2 μm) coating with minimal bridging of the fibre mats. The critical coating parameters when using this dip-coating technique have been discussed in detail. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Coatings; Dip coating; Sol–gel processes; ZrO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; Fibres

---

## 1. Introduction

The development of ceramic fibre reinforced ceramic matrix composites (CMCs) is a promising alternative to monolithic ceramics for obtaining structural materials combining high-temperature capability, toughness and damage-tolerance. The incorporation of the reinforcing fibres into the ceramic matrix provides the ceramic–ceramic composite body with a degree of ‘pseudo-ductility’, preventing catastrophic crack growth by such mechanisms as fibre debonding, fibre pull-out and crack bridging.<sup>1</sup> In order to achieve these properties, the fibre–matrix interface must be sufficiently weak to deflect cracks and allow subsequent fibre pull-out, yet strong enough such that transverse composite tensile and shear strengths are not too low. In relation to the mechanical properties, the influence and the control of the interface structure is of critical significance to the successful development of these composites. By a careful adjustment of the interface system, the subsequent reactions and diffusion between the fibre and the matrix can be

controlled. Barrier layers at the fibre–matrix interface can, for example, improve the thermal stability of the fibres. Fibre coatings may also be needed for oxidation protection and as chemical reaction barriers.<sup>2,3</sup>

Although boron nitride (BN) based interface coatings have proven useful as a weak interface in various CMC formulations,<sup>4,5</sup> BN is unsuitable for high-temperature oxidising environments, which require an oxidation-resistant fibre/interface system for long-term use. Thus, oxide based fibre coatings which provide a weak interface with the fibre and/or matrix and which are non-reactive with respect to the oxide fibre and the various candidate oxide matrices, are desirable. Zirconia (ZrO<sub>2</sub>), which is known to be chemically inert in combination with certain other oxide materials,<sup>6</sup> is an important ceramic coating material for high-temperature structural applications. It has been studied as a fibre coating material for promoting crack deflection and debonding at the fibre–matrix interface of Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> composites.<sup>7,8</sup> Zirconia has also been shown to possess a unique degree of chemical stability and has high thermal expansion with respect to alumina and non-oxide ceramics.

Numerous approaches to coating ceramic fibres, including chemical vapour deposition (CVD),<sup>9–11</sup> sol–gel/organometallic coating<sup>12–15</sup> and polymer precursor

---

\* Corresponding author.

<sup>1</sup> Current Address: Unilever Research, Colworth House, Sharnbrook, Bedford MK44 1LQ, UK.

deposition,<sup>16,17</sup> have been investigated. The majority of these techniques do not apply the coating material to the fibre directly, but use precursor chemicals which are then converted to the coating material through in-situ reaction or subsequent heat treatment. In this respect, the cheapest and potentially quickest coating method would be to dip-coat fibres directly using a sol of the desired final coating material, thus, avoiding the need for additional reaction/heat treatment conversion stages. Although this simple dip-coating technique can be used readily to coat single fibres,<sup>18</sup> when fibre tows or woven fibres are considered, however, the coating process becomes more difficult due to the increased complexity of the fibre spatial arrangement. Fibres in close proximity will be more difficult to coat evenly, and bridging of the fibers by the applied coating sol is not an uncommon occurrence.<sup>15</sup> The original work of Hay et al.<sup>19,20</sup> on the dip-coating of fibre tows, overcame this problem of inter-tow adherence by extracting the immersed fibre tows to air through a less dense immiscible liquid. Native fibre wetting was the sole mechanism by which various sols coated monofilaments, and this produced very thin coatings. Thicker coatings could be achieved only by performing multiple dip-coating runs (in some cases as much as 13). This led to problems with the through-thickness coating uniformity, however, due to the spallation of the thin fibre coatings during multiple runs. The particular focus of this work was to employ both surfactants and an immiscible liquid when dip-coating, in order to deposit a zirconia sol particle coating on woven ceramic-fibre cloths in a single-step process.

## 2. Experimental procedure

### 2.1. Fibre preparation

Plain-woven alumina (Almax, Mitsui Mining Co., Japan) and 8-harness satin weave alumina-silica (Nexcel<sup>TM</sup> 720, 3M, USA) fibre mats were used as substrate materials. These fibres are two types of an ever growing number of 2D and 3D woven fibre architectures which are currently available.<sup>21</sup> Prior to coating, pre-treatment of the woven fibre mat was necessary. This entailed desizing by heating in air at 500°C for 1 h. The coating technique employed relies on electrostatic attraction in addition to wetting to increase the thickness of the deposited ZrO<sub>2</sub> sol particle layer on the fibre surface. In this work, the electrostatic attraction was engineered on both the ZrO<sub>2</sub> particle surface and the fibre cloth prior to any fibre-sol contact.<sup>22</sup> The sign of electrostatic charge depended on the type of zirconia used for coating. For acid-stabilised sols, as with the majority of zirconia sols used in this work, ammonia solution was used to impart a negative surface charge to the fibre. In some

cases, the coating process was enhanced further by the application of a surfactant to the fibre surfaces which improved the wettability of the fibre surface. The fibre mats were first immersed in a 1.5 wt% solution of an ammonium salt of polymethacrylic acid (Versicol KA21, pH 9, Allied Colloids, UK) which had been pH adjusted to pH 11.5 using additional ammonia solution. This solution imparted a net negative charge to the fibre surface. Adjusting the pH carefully, maximised the electrostatic attraction between the fibre surface and the positively charged zirconia particles in the coating sol. After this pre-treatment stage, the fibres were dried in air.

### 2.2. Zirconia sol preparation

Several zirconia sols have been employed here, both from commercial sources, and via the hydrothermal synthesis of zirconium acetate precursor. The commercial sols were investigated originally due to their low-cost and ease of availability, factors which are always of importance when considering the processing of materials.

(i) Nyacol<sup>TM</sup> zirconia (The PQ Corporation, USA) is an acetate stabilised ZrO<sub>2</sub> sol containing 20 wt% ZrO<sub>2</sub>. The pH of the as-received sol was 3.8 and the average particle size 5–10 nm. In this work, the pH of the Nyacol<sup>TM</sup> ZrO<sub>2</sub> sol was adjusted to pH 2 by adding hydrochloric acid. This was performed in order to maximise the electrostatic attraction between the positively charged zirconia particle surfaces and the negatively charged fibre surfaces.

(ii) An acetate-free Nyacol<sup>TM</sup> zirconia sol was produced by drying the as-received commercial sol in an oven at 100°C for 8 h to vaporise the water present, followed by grinding the resultant powder with a mortar and pestle. After firing to 600°C for 10 h to remove the excess zirconium acetate, the powder was then re-dispersed with water by ball milling followed by a pH adjustment to pH 2 using HCl additions.

(iii) A ZrO<sub>2</sub> sol was made from Degussa ZrO<sub>2</sub> powder (Degussa Ltd, UK), with an average particle size of 30 nm, which was dispersed in an aqueous solution (weight fraction of 25%) by ball milling for two days. From the manufacturer's data, the dispersed powder is stable in water at a pH of 5 to 6; for the purposes here, however, a maximised particle-fibre electrostatic attraction was required. Hence, the pH value of the ZrO<sub>2</sub> sol was adjusted to pH 2 using hydrochloric acid.

In addition, a ZrO<sub>2</sub> sol was synthesised “in-house” using hydrothermal processing, as shown in Fig. 1. Commercial zirconium acetate solution ZrO(CH<sub>3</sub>COO)<sub>2</sub> (MEL<sup>®</sup> Chemicals, UK) was used as the precursor material. The zirconium acetate solution was placed in an autoclave (Berghof, Germany) and heated to 220°C under autogenous pressure for 2 h. The hydrolysis product was a zirconia sol, i.e. colloidal ZrO<sub>2</sub> particles, suspended in an acetic acid solution. This sol was then dried in an oven for 8 h at 80°C and the

resultant powder cake ground to a fine powder using a mortar and pestle. The powder was then calcined in an air muffle furnace at 600°C for 4 h to remove any residual zirconium acetate. The powder was then redispersed in an aqueous solution to the required concentration by ball-milling. The calcined and redispersed sol solution had a measured modal particle size of 50 nm and the pH of the solution was in the range of 2–3, indicating that the zirconia sol particles had retained an adsorbed layer of  $H^+$  ions throughout the calcining procedure. The pH value of the  $ZrO_2$  sol was adjusted to pH 2 using small additions of hydrochloric acid in order to maximise the  $ZrO_2$  to fibre electrostatic attraction.

### 2.3. Fibre mat coating procedure

The coating stage involved firstly the immersion of the fibre mats into the  $ZrO_2$  sol under vacuum. This served to outgas the fibre mat and encourage the  $ZrO_2$  sol to infiltrate fully the woven fibre architecture. The immersed fibre mats were extracted to air through a less dense immiscible liquid (octanol) floating above the zirconia sol.

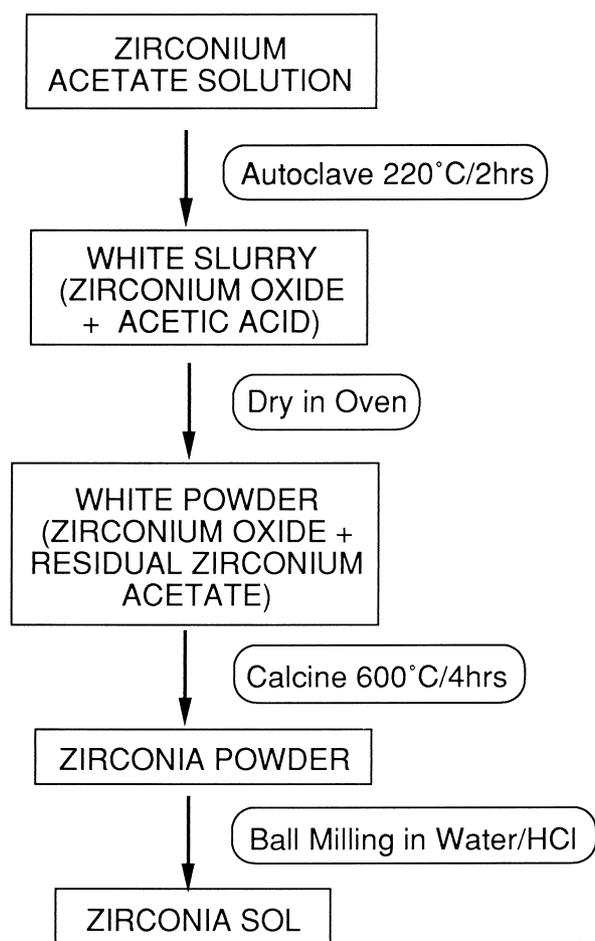


Fig. 1. Flow chart showing the production of zirconia powder by hydrothermal synthesis.

The favourable wetting characteristics of this immiscible liquid with respect to the sol particles enabled any bridging of adjacent coated fibres to be minimised on withdrawal from the sol.<sup>20</sup> After coating, the fibre mats were dried in air and then fired in a furnace at 600°C for 1 h to enhance the cohesion of the  $ZrO_2$  coating layer and improve its adhesion to the fibre surface. A schematic diagram of the  $ZrO_2$  coating process is shown in Fig. 2.

### 2.4. Specimen characterisation

Qualitative phase analysis of the zirconia powder which was synthesised by the hydrothermal process was undertaken using a Philips PW 1050/25 X-ray diffractometer (XRD) with  $CuK\alpha$  radiation.

A specimen for transmission electron microscopy (TEM) characterisation was prepared from the hydrothermal  $ZrO_2$  sol by the following procedure: firstly, a small sample of the sol was diluted with de-ionised water in a ratio of about 10 parts water to 1 part  $ZrO_2$ ; secondly, a copper grid with a thin carbon film supported on it was dipped into this diluted sol and then withdrawn carefully to retain a number of  $ZrO_2$  particles dispersed over the surface of the carbon film; finally, the grid was placed on top of a piece of filter paper to dry. These  $ZrO_2$  particles were then characterised using a Philips CM20 TEM with bright field

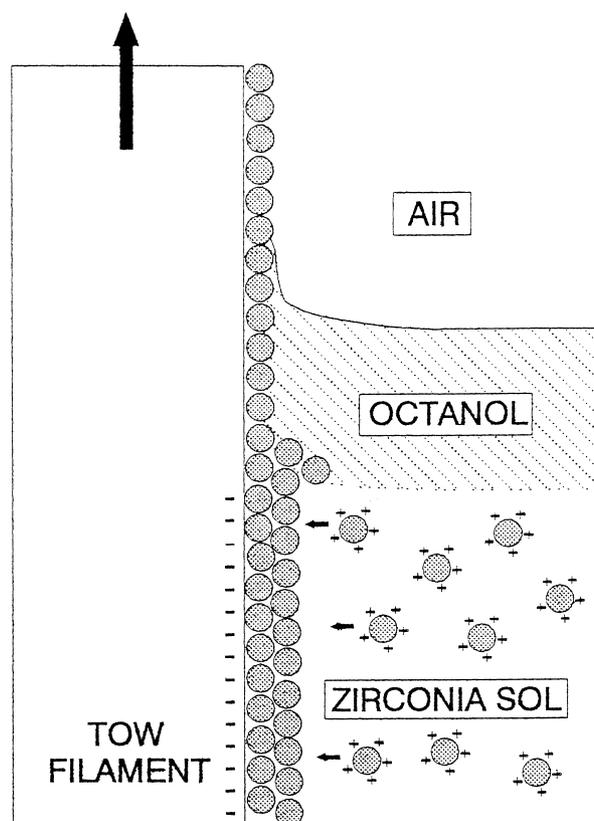


Fig. 2. Schematic diagram of zirconia coating on fibre mat using dip-coating technique.

imaging, selected area diffraction (SAD), and energy dispersive X-ray analysis (EDS).

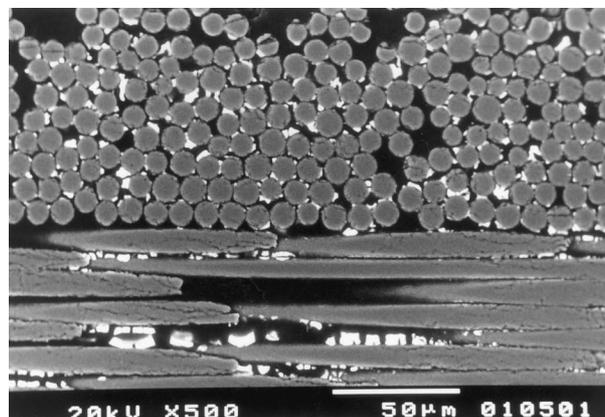
To prepare the coated fibre mat samples for cross-sectional scanning electron microscopy (SEM), each fibre mat sample was placed in a vacuum chamber and vacuum-impregnated with Epofix resin (Struers Tech A/S, Denmark). It was then left to harden overnight. The resin infiltrated fibre mat samples were then cross-sectioned using a diamond saw and then remounted using cold mounting powder with liquid hardener (MetPrep Ltd, UK). The mounted samples were ground and polished to a 1  $\mu\text{m}$  finish, and then gold coated prior to examination using SEM (JEOL 5410, Japan).

### 3. Results

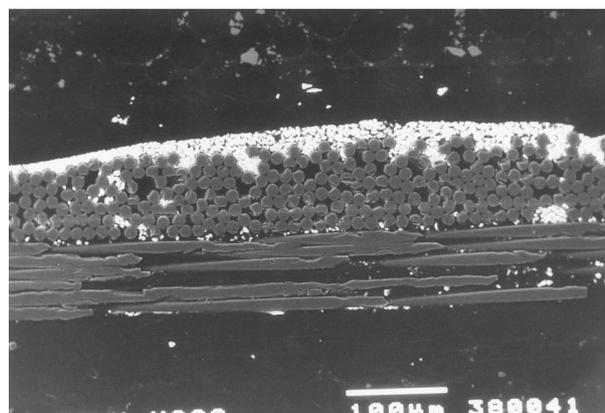
#### 3.1. Zirconia coating onto woven fibre mats using commercial sols

The results from the use of Nyacol™ zirconia colloidal sol to coat fibre mats are shown in Fig. 3. The micrograph in Fig. 3a shows that the  $\text{ZrO}_2$  sol was able to infiltrate the majority of the intra-tow regions of fibre mat. There were no fibres, however, which contained a uniform coating layer, indicating that inadequate wetting of the fibres had occurred on immersion and that non-uniform removal of excess sol occurred on extraction to air. The deposited zirconium acetate-based sol contained many cracks due to the loss of acetates during the post-coating firing stage. This result is similar to previous work reported by Trusty<sup>25</sup> who attempted to coat woven fibre mats with zirconium acetate solution and found that instead of coating the fibres, the acetate completely filled the inter-fibre regions and subsequently cracked on conversion to zirconia during the post-coating firing stage. These data suggest that when the precursor contains excessive chemicals which are subsequently removed at elevated temperatures, this process leads to shrinkage of the deposited zirconia and, therefore, non-uniform coatings on the fibre mat.

It was decided, therefore, to attempt to remove as much acetate from this Nyacol™ sol in order to minimise this shrinkage problem and to study also the effect of a reduced zirconium acetate concentration on the ability of the sol to wet the fibre surfaces. After the coating procedure was performed with the calcined and re-dispersed Nyacol™ zirconia sol, however, the SEM results showed that only a few zirconia particles were able to infiltrate the intra-tow regions of the fibre mat. Most of the zirconia remained on the outer surfaces of fibre mats [see Figure 3(b)]. This is because the particle size of the zirconia had increased dramatically from the 5–10 nm range to  $\approx 4 \mu\text{m}$  during the drying and calcination stages. The hard agglomerates formed could not be broken down during re-milling, and hence, the resultant powder dispersion contained particles that were too large for adequate infiltration.



(a)



(b)

Fig. 3. SEM backscattered electron image of zirconia coating using Nyacol™ zirconia colloidal sol. (a) Sol used as-received, showing many cracks present in the zirconia layer; (b) calcined and re-dispersed sol, showing most of zirconia remaining on the outer surface of the fibre mat.

Following on from this result, it was decided to use a Degussa zirconia powder which could be dispersed in water to form a sol. From the manufacturer's data, a stable, aqueous-based sol can be produced in the pH range 5–6. In order to increase the positive surface charge on the zirconia particles, however, the pH of the sol was adjusted to pH 2 using HCl additions. This process can be exploited more readily in such particulate sols in aqueous, than with chemical precursor-based sols. The SEM results in Fig. 4 show that infiltration of the preforms was possible, with some evidence of fibre wetting. Coatings were not uniform, however, and there was much evidence of fibre bridging as a result of inadequate sol displacement by the octanol.

#### 3.2. Zirconia coating onto woven fibre mats using hydrothermal sol

##### 3.2.1. Zirconia synthesised by hydrothermal process

On phase analysis of zirconia synthesised in this work using X-ray diffraction, the trace in Fig. 5 shows that the zirconia is baddeleyite which has a monoclinic crystal

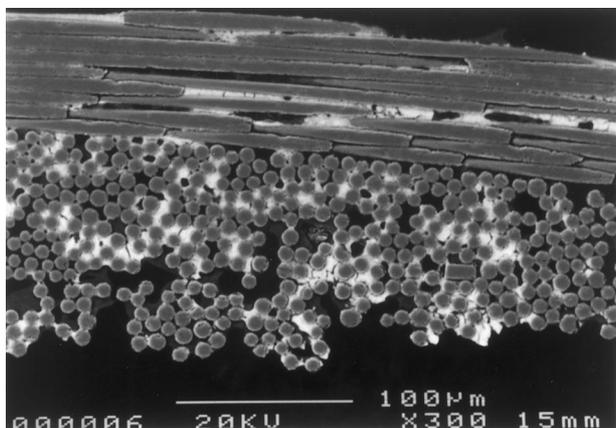


Fig. 4. SEM backscattered electron image of zirconia coating using Degussa zirconia powder which was dispersed in aqueous to form a sol, showing the non-uniform coating and intra-fibre tow bridging.

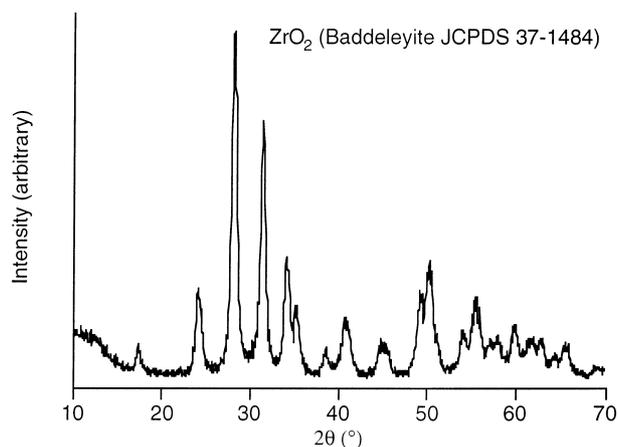


Fig. 5. XRD pattern of zirconia powder synthesised by hydrothermal process, showing that the zirconia is baddeleyite with a monoclinic crystal structure.

structure. Fig. 6(a) shows a TEM image of some particles from the  $ZrO_2$  sol. As may be seen in this image, most particles are rounded with dimensions in the range of 15–50 nm, although some are slightly elongated rather than spherical in morphology; these are usually clustered in small groups. The identification of these particles as  $ZrO_2$  was also confirmed by both selected area diffraction and EDS. Fig. 6(b) shows a selected area diffraction pattern from the particles shown in Fig. 4(a). The ring radii for this pattern correspond very well with those that would be expected for monoclinic  $ZrO_2$ . Fig. 4(c) shows an EDS trace from one of the small clusters of particles shown in Fig. 4(a). This trace shows strong peaks for Zr and O. The peaks for Cu and C arise from stray scattering of X-rays from the copper grid and the carbon film, respectively.

### 3.2.2. Zirconia coating using hydrothermal sol

It has been recognised that the key factors in the dip-coating process are the wetting of the fibres by the  $ZrO_2$

sol and the electrostatic attraction between the fibre surface and  $ZrO_2$  sol particles. Fig. 7 shows an SEM back-scattered electron image (BEI) of the hydrothermally synthesised  $ZrO_2$  sol particle coating on a fibre mat. The light regions around the fibres correspond to the presence of  $ZrO_2$ , indicating a coating thickness of approximately 1–2  $\mu m$  with minimal inter-fibre bridging. The average particle size of this hydrothermally synthesised zirconia was therefore small enough to infiltrate in-between the fibre mat intra-tow regions unlike the case with calcined acetate-based Nyacol<sup>TM</sup>.

The control of each stage during the coating process is very important, as it effects greatly the ability of the zirconia to coat evenly each fibre tow filament. In order to determine the critical coating parameters when using this hydrothermally produced sol, a series of experiments were conducted to examine several aspects of the process in more detail.

*3.2.2.1. The effect of ammonia immersion and drying time.* Immersing the fibre mats into ammonia based Versicol solution (pH 11.5) served to create a negative charge on the fibre surface and also to improve the wetting between fibre and zirconia sol. Unlike previous work on monofilament Saphikon alumina single crystal fibres which were found to be dry in less than 1 min after ammonia immersion,<sup>18</sup> fibre mats needed to be dried for several hours at least. The experimental results in this work showed that if the individual fibre surfaces were not totally dry, then when the fibre mat was dipped into the zirconia sol, a gel would form between the individual fibres where some ammonia solution still remained, as shown by the SEM BEI micrograph in Fig. 8.

*3.2.2.2. The effect of fibre mat architecture.* Plain woven Almax (alumina) and 8 harness satin weave Nextel (mullite) fibre mats were both coated using this technique. It was thought originally that the more tightly woven Almax fibre mat would be more difficult to coat than the looser 8 harness satin woven Nextel fibres. On reference to the SEM BEI micrographs in Fig. 9, however, it can be seen that both woven fibre architectures are equally well coated using this method.

*3.2.2.3. The effect of octanol.* During the coating process, in order to prevent intra-tow filament adherence, the immersed fibre mat was extracted to air through a less dense immiscible liquid (octanol) which floated above the  $ZrO_2$  sol. During extraction, as the fibres moved from the sol region to the octanol layer, the octanol attempted to displace the sol coating. All of the coating was displaced, except a thin layer which remained electrostatically attracted to the fibre surface (see Fig. 7). If octanol was not employed as part of the process, however, excessive bridging of the fibres occurred, as can be seen in the SEM BEI micrographs in Fig. 10.

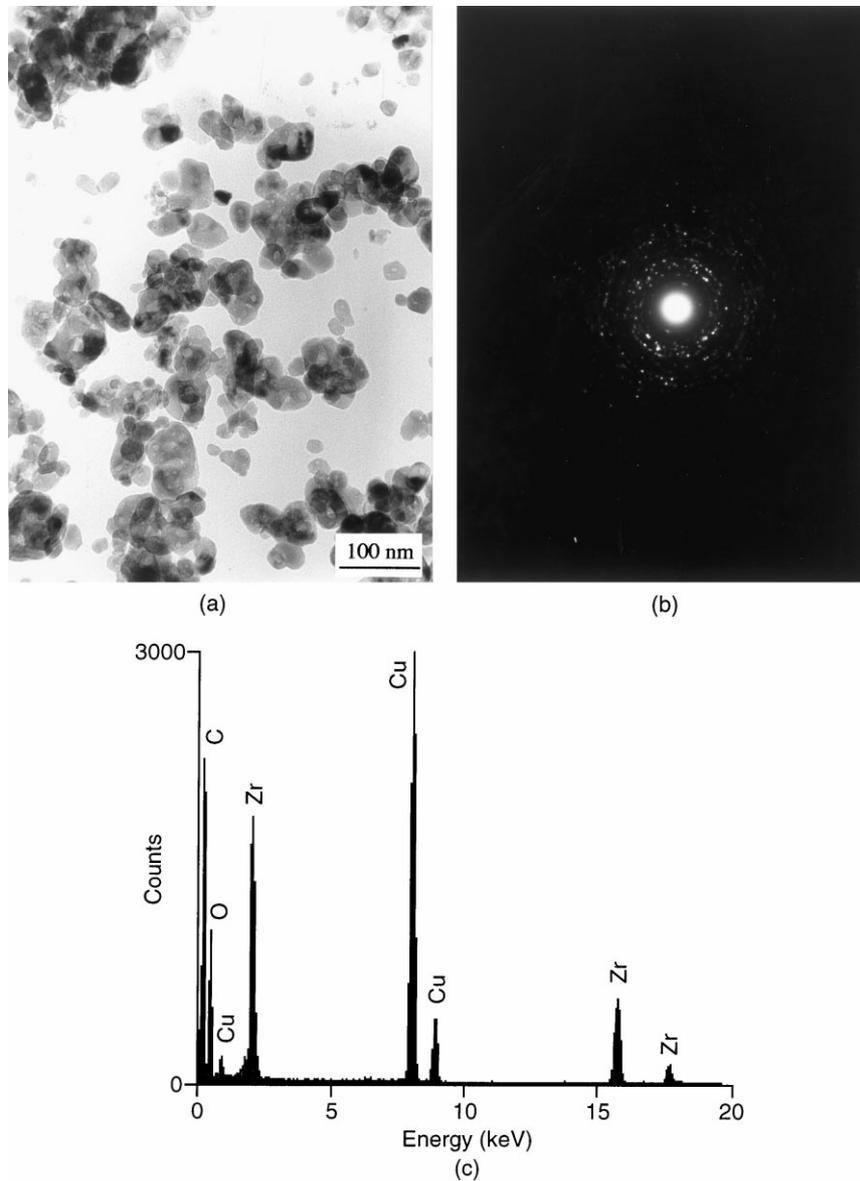


Fig. 6. TEM micrograph of hydrothermally synthesised zirconia powder. (a) TEM bright field micrograph; (b) diffraction pattern; (c) EDS of particle cluster.

**3.2.2.4. The effect of vacuum.** When the fibre mats were immersed into either ammonia solution, Versicol solution, or the zirconia sol, on the application of a vacuum the capillary pressure difference across the curved fibre surfaces was increased which led to enhanced infiltration of the liquid medium into the intra-tow regions. The SEM BEI micrograph in Fig. 11 shows that when the coating process was performed in a poor vacuum, the final zirconia coating remained on the outer surface of fibre mats and was not able to infiltrate in-between the fibre tows.

**3.2.2.5. The effect of zirconia sol concentration.** The volume fraction of  $ZrO_2$  particles present in the coating sol was found to be an important parameter when considering the final thickness of the deposited coating

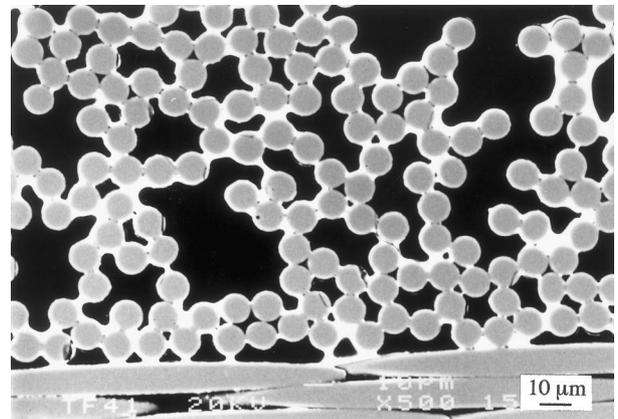


Fig. 7. SEM backscattered electron image of a fibre mat coated using hydrothermally synthesised zirconia, showing a  $ZrO_2$  coating thickness of approximately 1–2  $\mu m$  (light region) around the fibres.

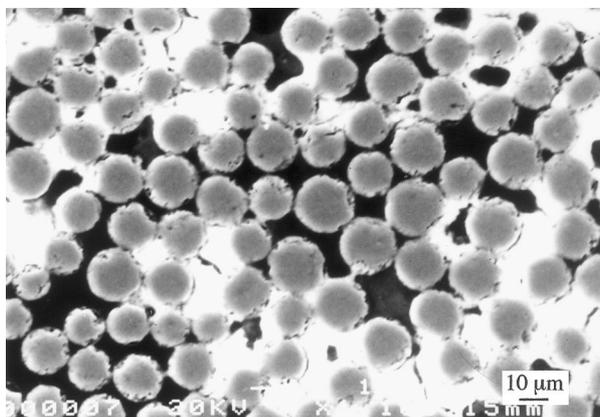


Fig. 8. SEM backscattered electron image of zirconia coating fibre mat which was dried in air for 1 h after immersion in ammonia, showing the formation of a zirconia gel between the individual fibres.

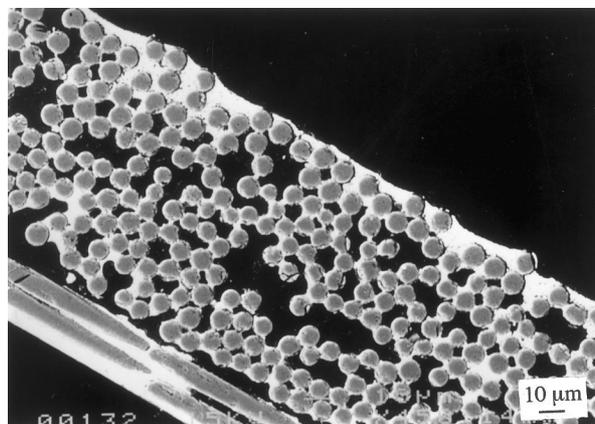
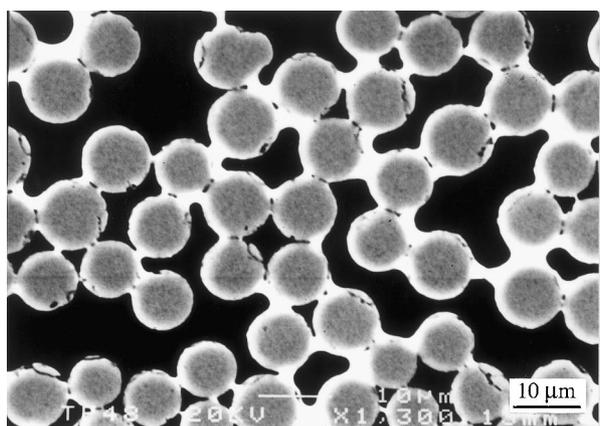
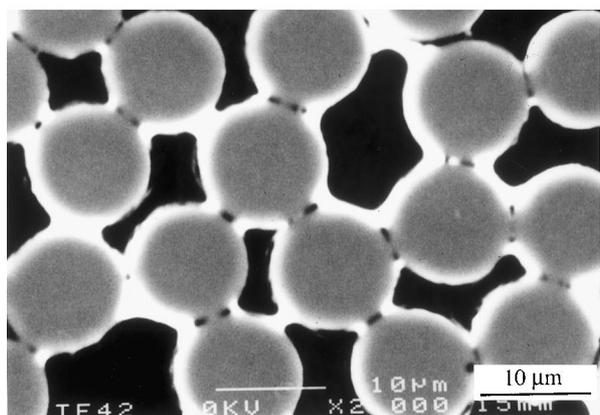


Fig. 10. SEM backscattered electron image of zirconia coating without the use of octanol, showing the extensive fibre bridging by the zirconia.



(a)



(b)

Fig. 9. SEM backscattered electron image of zirconia coating fibre mat, (a) Almax alumina fibre; (b) Nextel mullite fibre, showing that both woven fibre architectures are equally well coated with  $ZrO_2$ .

layer. Coating experiments were performed using sols with 10, 25 and 30 wt% of  $ZrO_2$  in aqueous solution. It was found that when using a 10 wt%  $ZrO_2$  sol, the thin coating layer which adhered to the fibre was subsequently removed by the octanol [see Fig. 12(a)]. When

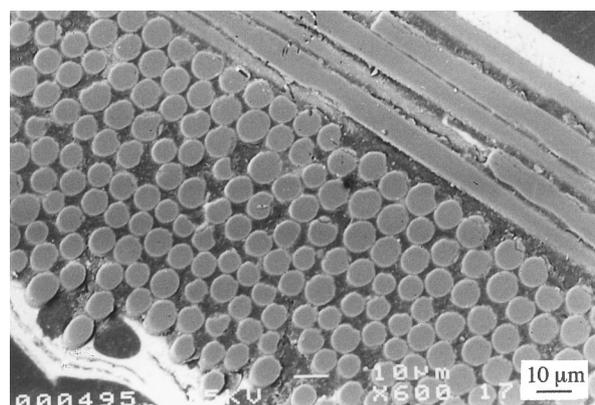


Fig. 11. SEM backscattered electron image of zirconia coating without the use of a vacuum to aid sol infiltration, showing that the zirconia coating only remained on the outer surface of fibre mats.

using a 30 wt% sol, however, the excessive amount of  $ZrO_2$  present between the fibres could not be removed adequately by the octanol, leading to extensive fibre bridging [see Fig. 12(b)]. For this particular system, therefore, a 25 wt%  $ZrO_2$  sol was found to be the optimum for the successful coating of the woven fibre mats (see Fig. 7).

#### 4. Discussion

It is believed that the successful zirconia coating technique depends on (i) the characteristic of zirconia particles in sol and (ii) the wetting of the fibre by zirconia sol and the electrostatic attraction between the fibre surface and  $ZrO_2$  sol particles.

##### 4.1. Wetting and infiltration of fibre mats

The dip-coating process generally relies on the wetting behaviour of the fibre by the sol. In order to optimise

the coating of fibre mats, the sol employed is required to wet the fibre surfaces. The general Young–Dupr e equation describes this wetting behaviour:

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos \theta \quad (1)$$

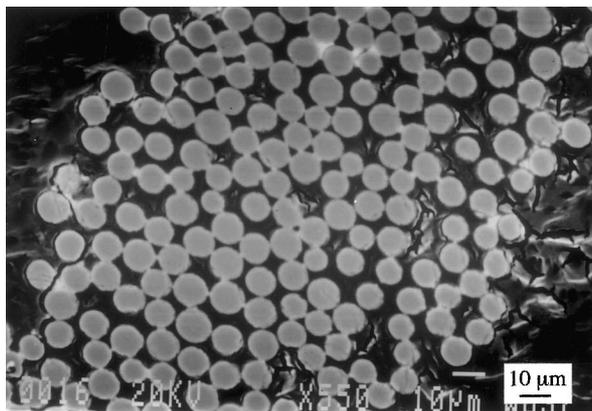
where  $\theta$  is the contact or wetting angle and  $\gamma_{sl}$ ,  $\gamma_{sv}$ , and  $\gamma_{lv}$  are the energies of the solid–liquid, solid–vapour and liquid–vapour interfaces respectively. The wettability is often defined as the ability of a liquid to wet a solid surface, i.e. to give an even, continuous film over the solid surface. A system is thought to be wetted when the contact angle  $\theta$  is less than  $90^\circ$ , ideally  $0^\circ$ , and non-wetted when  $\theta$  is greater than  $90^\circ$ . In order to optimise wetting,  $\gamma_{sl}$  can be minimised for a given  $\gamma_{sv}$  and  $\gamma_{lv}$  by minimising the contact angle,  $\theta$ . This can be achieved through the use of surfactants which can adsorb to both the solid–liquid and liquid–vapour interfaces, therefore lowering these interfacial energies. In this work, the surfaces of the fibres used at early stage were pre-treated with both ammonia solution and a surfactant (Versicol KA21) in order to maximise particle–fibre electrostatic attraction and to improve fibre wettability by lowering

$\gamma_{sl}$ , respectively. The surfactant on the fibre surfaces enables the water present in the sol to wet each fibre surface, but more importantly this wetting process introduces zirconia particles into the vicinity of the fibre surface. The particles can then be deposited onto the fibres by electrostatic attraction-enhanced hetero-coagulation, thus forming the coating whilst the mat is immersed.

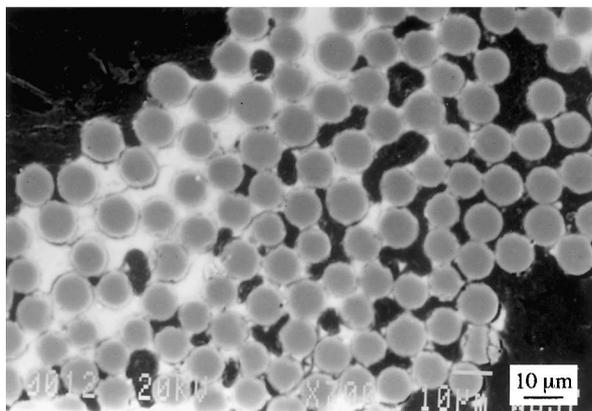
When considering the basic mechanism by which a liquid wets a fibre, more than just the contact angle is involved in the process, since the liquid must also penetrate in between the fibres of the fabric. In this respect, the curvature of the fibre surface also affects the wetting process. The surface energy,  $\gamma_{sl}$ , causes the generation of a pressure difference,  $\Delta P$ , across the convex fibre surface with respect to a planar surface. Eq. (2) below shows how capillary pressure is related to radius of curvature of the fibres,  $r$ , and the energies of the solid–vapour and solid–liquid interfaces<sup>23</sup>:

$$\Delta P = \frac{2(\gamma_{sv} - \gamma_{sl})}{r} \quad (2)$$

Thus, this equation shows that there is a net pressure to transfer material from the solution to the fibre surface. As illustrated in Fig. 13, if  $\Delta P$  is negative (which would occur if the contact angle were greater than  $90^\circ$ ), the liquid will tend not to penetrate between the fibres. Conversely, for contact angles below  $90^\circ$  and a positive  $\Delta P$ , liquid will penetrate these inter fibre regions more readily [Fig. 13(b)]. For optimum coating efficiency, therefore, a maximised pressure difference can be achieved by increasing the wettability of the fibre–sol surface using surfactants (thus reducing  $\gamma_{sl}$ ), by applying an external pressure to the whole system in the form

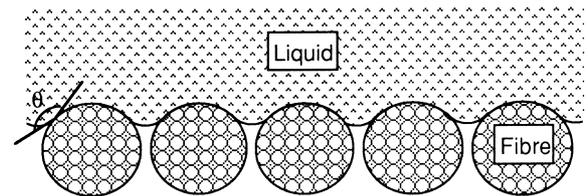


(a)

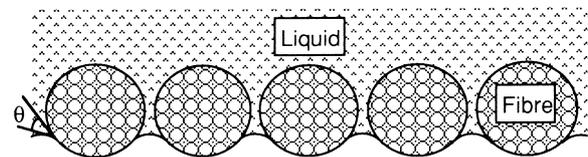


(b)

Fig. 12. SEM backscattered electron image of zirconia coating with using different solids loadings sols. (a) 10 wt% zirconia; (b) 30 wt% zirconia.



(a)



(b)

Fig. 13. Schematic of liquid infiltration of fibre mats. (a)  $\Delta P > 0$  and  $\theta > 90^\circ$ ; (b)  $\Delta P < 0$  and  $\theta < 90^\circ$  (after Adamson<sup>23</sup>).

of a vacuum (which would increase  $\gamma_{sv}$ ), and/or by decreasing the radius of curvature through a reduction in fibre diameter. For the woven fibre systems used in this work, the application of a vacuum has an additional advantage in that it also reduces the amount of entrapped air in the fibre mat thus aiding the infiltration process.

In addition to a high capillary pressure difference, the rate of capillary penetration,  $v$ , is important for adequate wetting of all fibre surfaces. This parameter is dependant primarily on the viscosity of the liquid,  $\eta$ , as shown in Eq. (3) below:<sup>23</sup>

$$v = \frac{\gamma_{lv} \cos \theta}{\eta} \quad (3)$$

According to this equation, the lower the viscosity of the liquid, the higher the rate of capillary penetration. With the hydrothermally synthesised sols used in this work, the lower concentration sols had lower viscosities and were found to outgas more rapidly on the application of a vacuum. This rapid outgassing was attributed to their higher rate of capillary penetration and was thought to enhance the wetting process.

Theoretically, the coating of a fibre by a liquid can occur only if  $\theta$  is sufficiently low to allow the fibre to remain wetted when it is removed from the liquid bath. In practice, however, the low value of  $\theta$  and optimised wetting conditions, coupled with the fibre tow architectures used produced an additional problem. Even though complete infiltration was achieved, on removal of the fibre from the liquid, excess sol would remain entrapped between the fibre interstices due to intra-tow filament adherence. This was an indication that the dewetting process was not adequate enough to leave only a thin coating of wetted material on the fibre surface. In order to address this problem, intra-tow filament adherence was reduced substantially by extracting the fibres from the sol to air through a less dense immiscible liquid (i.e. octanol). The relevance of this immiscible liquid is outlined in the following sequence of events:

- i. The tow filaments have an electrostatically attracted coating of zirconia whilst in the zirconia sol.
- ii. The filaments are extracted through the octanol layer which attempts to displace the zirconia sol. A layer of zirconia still remains adhered to the fibre surface after this octanol stage, however, due to the combined mechanisms of wetting and electrostatic attraction
- iii. The octanol wets the sol-air interface leaving a thin layer of octanol on the zirconia which keeps the filaments apart whilst the zirconia layer dries.

For the events in (ii) and (iii) to occur, the following wetting relationships must hold:

$$\gamma_{\text{fibre-octanol}} > \gamma_{\text{fibre-sol}} + \gamma_{\text{sol-octanol}} \quad (4)$$

$$\gamma_{\text{sol-air}} > \gamma_{\text{octanol-sol}} + \gamma_{\text{sol-octanol}} \quad (5)$$

where  $\gamma$  are the relevant interfacial energies. This immiscible liquid technique has been used most recently by Hay et al.<sup>20,26</sup> to coat alumina tows with various sols, in which the coating relied solely on the mechanism of wetting to determine the adherence of sol coating on fibre. In this work, the distinct difference is that the woven fibre mats were preconditioned electrostatically prior to coating. The main advantage of this preconditioning is that a thicker, more uniform layer of sol, i.e. zirconia, can be applied in a single run. The electrostatic attraction between the positively charged zirconia particles and the negatively charged fibre surface affects the coating thickness. This electrostatic attraction has been engineered deliberately.

Although it has been recognised that the key factors in the dip-coating process are the wetting of the fibres by the  $\text{ZrO}_2$  sol and the electrostatic attraction between the fibre surface and  $\text{ZrO}_2$  sol particle, the experimental results have also shown that the type of zirconia sol used in the coating process is of paramount importance to the success of the technique.

It has been shown that it is very important to use pure zirconia for woven fibre dip coating. The problem of using sols which are not colloidal dispersions in water, but rather comprise chemical precursors such as zirconium acetate<sup>25</sup> or zirconium carbonate,<sup>24</sup> is that excess chemicals need to be removed by firing at elevated temperatures after the coating stage. This removal of chemicals during firing promotes cracking of the zirconia layer as the precursor shrinks. The stability of the sol is another key factor for zirconia coating. For example, although a Degussa zirconia sol could be made by dispersing pure zirconia particles of size 30 nm in water, the sol did not produce an adequate coating on the fibres. This is due to the fact that these zirconia particles are usually stable in the pH range 5–6 when dispersed in water, but the pH of the sol was adjusted to pH 2 during coating in an attempt to maximise particle-fibre electrostatic attraction. This altering of the pH may have reduced substantially the stability of the particles in suspension, causing them to lose their discrete nature and agglomerate. Hence, during the coating process, although these relatively larger zirconia agglomerates would be able to infiltrate the intra tow regions, they would not be able to deagglomerate and deposit as a thin coating on the fibre surfaces. For the hydrothermal zirconia sol, the average particle size was measured to be ca. 50 nm after drying and calcination. In addition, on redispersion of such hydrothermally produced zirconia particles in water, the pH of the resultant stable sol was in the range 2–3. This is due to the fact that the zirconia particles retained a layer of adsorbed  $\text{H}^+$  ions

during the calcination stage. Hence, each discrete zirconia particle has a positive surface charge in water, which is dissimilar enough to the negatively charged fibre surfaces and, therefore, promotes a maximised particle–fibre electrostatic attraction. It is suggested that these unique properties of the hydrothermally synthesised zirconia have enabled it to be used successfully in the coating of woven fibre mats using this dip-coating method. Moreover, as this method does not require sophisticated apparatus, it has great potential to be used as a standard coating technique with woven fibre preforms.

## 5. Conclusions

A study of the dip-coating of woven fibre mats with several different zirconia sols (both commercial and non-commercial) has been undertaken. It has been found that only the ZrO<sub>2</sub> sols synthesised hydrothermally “in-house” from zirconium acetate solution have the desired properties for the successful dip-coating of oxide woven fibre mats.<sup>24</sup> The effectiveness of the octanol in displacing the excess sol coating from the fibre surfaces was found to relate directly to the initial volume fraction of zirconia in the coating. A 25 wt% dispersion of zirconia in water proved to be the optimum for this system, enabling the fibre coating stage to be performed in a single step. This result is important as it will enable this rapid, economical technique to be used as a general zirconia coating procedure in the fabrication of oxide woven fibre reinforced CMCs.

## Acknowledgements

The authors wish to thank the Engineering and Physical Science Council (EPSRC) and the IRC in Materials for funding this work. Professors M. H. Loretto and I. R. Harris are acknowledged for provision of laboratory facilities in the IRC and the School of Metallurgy and Materials, respectively. The authors are grateful also to Dr. Ian MacLaren for his assistance with the TEM studies.

## References

- Evans, A. G. and Marshall, D. B., High toughness ceramics and ceramic composites. *Progress in Materials Science*, 1989, **33**, 85–90.
- Wang, Y. Q., Zhou, B. L. and Wang, Z. M., Oxidation protection of carbon fibres by coatings. *Carbon*, 1995, **33**, 427–433.
- Westwood, M. E., Webster, J. D., Day, R. J., Hayes, F. H. and Taylor, R., Review oxidation protection for carbon fibre composites. *J. Mat. Sci.*, 1996, **31**, 1389–1397.
- Jessen, T. L. and Bender, B. A., Layered BN-coated/as-received unidirectional fibre CFCCs with enhanced mechanical performance. *Ceram. Eng. Sci. Proc.*, 1994, **15**, 311–318.
- Sheldon, B. W., Sun, E. Y., Nutt, S. R. and Brennan, J. J., Oxidation of BN-coated SiC fibres in ceramic matrix composites. *J. Am. Ceram. Soc.*, 1996, **79**, 539–543.
- Lundberg, R., Pejryd, L., Butler, E. G., Ekelund, M. and Nygren, M., Oxidation resistant interphases for all-oxide ceramic composites. In *6th European Conference on Composite Materials*, Bordeaux, France, 20–24 September 1993.
- Lundberg, R. and Eckerbom, L., Design and processing of all-oxide composites, in Ceramic Transactions. In *Proceeding of High-Temperature Ceramic–Matrix Composites, II Manufacturing and Materials Development*, ed. A. G. Evans and Ronaslain. American Ceramic Society, Westerville, OH, USA, 1995, pp. 95–104.
- Davis, J. B., Lövfavander, J. P. A. and Evans, A. G., Fibre coating concepts for brittle-matrix composites. *J. Am. Ceram. Soc.*, 1993, **76**, 1249–1257.
- Ha, J. S., Chawla, K. K. and Engdahl, E. E., Effect of processing and fibre coating on fibre–matrix interaction in mullite fibre–mullite matrix composites. *Mat. Sci. and Eng.*, 1993, **A161**, 303–308.
- Griffin, C. J. and Kieschke, R. R., CVD processing of fibre coatings for CMCs. *Ceram. Eng. Sci. Proc.*, 1995, **16**, 425–432.
- Westwood, M. E., Webster, J. D., Day, R. J., Hayes, F. H. and Taylor, R., Review oxidation protection for carbon fibre composites. *J. Mat. Sci.*, 1996, **31**, 1389–1397.
- Subramanian, R. V. and Nyberg, E. A., Zirconia and organotin-titanate film formation on graphite fibre reinforcement for metal matrix composites. *J. Mater. Res.*, 1992, **7**, 677–688.
- Deslandes, Y. and Sabir, F. N., Inhibition of oxidation of carbon fibres by sol–gel coatings. *J. Mat. Sci. Lett.*, 1990, **9**, 200–202.
- Kubeckova, M., Sedlar, M. and Matejec, V., Characterization of sol–gel derived coatings on optical fibres. *J. Non-Crystalline Solids*, 1992, **147 & 148**, 404–408.
- Meier, B., Grathwohl, G., Spallek, M. and Pannhorst, W., Sol–gel coatings on ceramic fibres for ceramic matrix composites. *J. Eur. Ceram. Soc.*, 1992, **10**, 237–243.
- Hurwitz, F. I., Hyatt, L., Gorecki, J. and D’Amore, L., Silsesquioxanes as precursors to ceramic composites. *Ceram. Eng. Sci. Proc.*, 1987, **8**, 732–743.
- Wang, Y. Q., Wang, Z. M., Yang, J. Y., Zhang, F. Q. and Zhou, B. L., SiC coating on carbon fibres by a solution coating process. *Composites Manufacturing*, 1995, **6**, 103–106.
- Pearce, D. H., Jickells, A. J. and Ponton, C. B., Zirconia coated alumina fibres as a reinforcement for alumina. In *Third Euro-Ceramic*, Vol. 1, ed. P. Durán and J. F. Fernández. Faenza Editrice Ibérica S.L, Spain, 1993, pp. 231–236.
- Hay, R. S. and Hermes, E. E., Sol–gel coatings on continuous ceramic fibres. *Ceram. Eng. Sci. Proc.*, 1990, **11**, 1526–1538.
- Hay, R. S., Sol–gel coating of fibre tows. *Ceram. Eng. Sci. Proc.*, 1991, **12**, 1064–1074.
- Ko, F. K., Preform fiber architecture for ceramic-matrix composites. *Am. Ceram. Soc. Bull.*, 1989, **68**, 401–414.
- Brownie, P. M., Ponton, C. B., Marquis, P. M. and Butler, E. G., Electrostatic deposition of ceramic sol particles on ceramic substrates. *Ceram. Eng. Sci. Proc.*, 1993, **14**(9–10), 717–724.
- Adamson, A. W., *Physical Chemistry of Surfaces*, 4th edn. Wiley, New York, 1982.
- Gu, X., Trusty, P. A. and Butler, E. G., Zirconia coating on 2-dimensional woven fibre mats. In *Proceeding of the 7th International Conference on Fibre Reinforced Composites (FRC '98)*, ed. A. G. Gibson. Woodhead Publishing Limited, Cambridge, UK, 1998, pp. 256–263.
- Trusty, P.A., *The Development of Oxide/Oxide Ceramic Fibre Composites. Progress Report III to DRA*. IRC in Materials for High Performance Applications, The University of Birmingham, UK, 1994, pp. 5–7.
- Hay, R. S., Petry, M. D., Keller, K. A., Cinibulk, M. K. and Welch, J. R., Carbon and oxide coating on continuous ceramic fibers. *Mater. Res. Soc. Symp. Proc.*, 1995, **365**, 377–382.