JOURNAL OF MATERIALS SCIENCE **39** (2004) 851–859

TiO_2 coatings on silicon carbide and carbon fibre substrates by electrophoretic deposition

A. R. BOCCACCINI[*,†], P. KARAPAPPAS[*,†], J. M. MARIJUAN[*]
[*]*Department of Materials and* [†]*Centre for Composite Materials, Imperial College London, Prince Consort Rd., London, SW7 2BP, UK*
E-mail: a.boccaccini@imperial.ac.uk

C. KAYA
Wolfson Centre for Materials Processing & Mechanical Engineering, Brunel University, Uxbridge, UB8 3PH, UK

Electrophoretic deposition (EPD) has been used to obtain TiO_2 coatings on three dimensional (3-D) SiC fibre (Nicalon®-type) and carbon fibre substrates. Colloidal suspensions of commercially available TiO_2 nanoparticles in acetylaceton with addition of iodine were used. The EPD parameters, i.e., deposition time and voltage, were optimised for each fibre type. Strongly adhered TiO_2 deposits with high particle packing density were obtained. Scanning electron microscopy observations revealed high penetration of the titania nanoparticles into the fibre preforms. The TiO_2 deposits were sintered at 800°C for 1 h in order to produce relatively dense and uniform TiO_2 coatings covering completely the SiC or carbon fibres. For the carbon fibre/TiO_2 system, an effort was made to produce a 3-D titania matrix composite by further infiltration of the porous fibrous preform with TiO_2 by slurry dipping and subsequent pressureless sintering. The 3-D carbon fibre reinforced TiO_2 matrix composites fabricated contained residual porosity, indicating further infiltration and densification steps are required to produce dense composites of adequate structural integrity. For SiC fibre fabrics, oxidation tests in air established the effectiveness of the TiO_2 coating as oxidation protective barrier at 1000°C. After 120 h the increase of weight due to oxidation of coated fibres was more than twice lower than that of the uncoated fibres. TiO_2 coated SiC fibre preforms are attractive materials for manufacturing hot gas filters and as reinforcing elements for ceramic matrix composites.

1. Introduction

Due to its high chemical durability and thermal stability as well as high hardness and wear resistance, titanium oxide, mainly in its rutile modification, is a candidate material for developing protective coatings on metallic and ceramic substrates [1–3]. Titania coatings have been also proposed as oxidation, corrosion and wear protection coatings for carbon fibres [4, 5], metallic fibres [6], light alloy substrates [3] and stainless steel sheets [7]. In recent research, titania has been also considered as an appropriate interfacial coating in carbon-carbon composites [8].

Oxide ceramics are good candidates for oxidation and corrosion protection of metallic, carbon and silicon carbide fibres. Oxide ceramic coatings on fibres and fibrous substrates have traditionally been produced by either chemical vapour deposition, slurry-dipping or sol-gel techniques [4, 5, 8–14]. There is however increasing interest in the use of electrophoretic deposition (EPD) in this field, as reported in the recent literature [6, 15–21]. EPD has been shown to be a versatile, effective and low cost technique to produce oxide coatings of controlled thickness and homogeneous microstructure on a wide range of substrates, including metallic and ceramic planar substrates, wires, individual fibres, filaments, fibrous structures and porous components [6, 7, 15–25]. EPD is based on the presence of small charged ceramic particles in a liquid, which, on the application of an electric field, will move to and deposit on an oppositely charged electrode, where the substrate to be coated is placed [22]. The theoretical basis of the EPD technique and its application in ceramic processing have been presented in comprehensive review papers [17, 22–24].

In this study, an EPD based process has been developed to produce titanium dioxide protective coatings on three-dimensional (3-D) SiC (Nicalon®-type) and carbon fibre performs. The aims have been twofold; (i) to provide high-quality protective coatings to enhance the oxidation and corrosion resistance of the fibres for high temperature applications, and (ii) to provide suitable fibre reinforcement elements to be used in titania matrix composites.

2. Experimental procedure

2.1. Materials

Two types of fibre substrates were investigated in this work. The SiC-based fibre preforms used were made of Nicalon®-type fibres of grade NL202. The preforms had thickness of 3 mm and were produced by overlapping 2-dimensional layers of randomly oriented fibres. Scanning electron microscopy (SEM) revealed that the diameter of the fibres in the as received condition was in the range 15–20 μm. The carbon fibres used were type T300, Torayca®, provided by Toray Ind., Tokyo, Japan. The nominal diameter of the as-received fibres was 10 μm, as determined by SEM images.

The titania powder used was TiO_2 grade P25 (Degussa AG, Germany), which is a very fine (fumed) powder of mean particle size 21nm and specific surface area of 50 m^2/g. It is produced by hydrolysis of gaseous metallic chloride ($TiCl_4$) under the influence of water and it is composed of about 70% anatase modification, the rest being rutile [26]. The same nanopowder has been used in previous studies to coat metallic fibres by EPD [6].

2.2. Electrophoretic deposition of coatings and characterisation

Titania coatings on both SiC and carbon fibre substrates were produced by electrophoretic deposition (EPD). The solution for EPD was prepared using 2,4-Pentandione (Acetylaceton) 99+% (Sigma-Aldrich. Co. Ltd.) as solvent with addition of iodine 99.999% (Aldrich Chemical Company, Inc.) in order to enhance particle charging in the solution. Similar suspensions have been used by other authors [27] to prepare $BaTiO_3$ films by EPD. After a trial-and-error approach, the optimal concentration of components in the solution was determined as: 0.5 g TiO_2, 0.04 g iodine in 50 ml acetylacetone. The stability of the solution was enhanced after sonically stirring for 15 min. After each electrophoretic deposition test, the solution was magnetically stirred for 3 min.

A borosilicate glass beaker was used as the container for the EPD cell. Both electrodes where hold by a tweezed-arm to enable them to be dipped into the prepared solution kept in the glass beaker. The distance between electrodes was 2 cm. The electrodes were connected to a D.C. power supply and a multimetre to enable measurement of electric data. In order to coat the SiC and carbon fibre substrates by EPD, these were placed as the cathode in the EPD cell, knowing that TiO_2 particles in this suspension would acquire positive charge, as determined in preliminary trials. The cross section of the fibre substrates and of the counter-electrodes (stainless steel sheets) was 1.5×1.5 cm^2.

In order to establish the best possible EPD parameters for obtaining high-quality and reproducible TiO_2 coating on the fibres, two series of tests were carried out for each fibre type. One set of experiments involved constant deposition time and different applied voltages of 30, 40 and 50 volts for SiC fibres and 5, 10, 15, 20, 25 and 30 V for carbon fibres. In the other experiment series, the applied voltage was kept constant and deposition time was varied from 1 to 4 min for the two fibre types. After EPD, the coated fibre preforms were carefully extracted from the solution and dried in a chamber at room temperature under controlled humidity atmosphere. The TiO_2 coatings were characterised by visual inspection and scanning electron microscopy (SEM) (Jeol T-200A and T-220A). For each fibre type, comparison of the results of both series of tests led to the optimal experimental conditions to produce the electrophoretic deposited TiO_2 coating of best quality in terms of adherence to the substrates, coating microstructure homogeneity, uniform coating thickness, degree of ceramic penetration into the fibrous structure and extent of microcracking upon drying.

Sintering of the EPD coatings was performed under controlled argon atmosphere with a flow rate of 20 ml/min. Heating and cooling rates were 10°C/min. Electric furnaces (Carbolite, Ltd.) were used for this purpose, and sintering was carried out at both 800 and 1000°C for 1 and 2 h dwelling time.

The microstructure of the samples after sintering was observed using SEM. High magnification observation of the sintered TiO_2 coatings was carried out with a LEO 1525 FEG-SEM in order to reveal the presence of residual porosity and microcracks in the sintered coatings. The crystalline structure of the coatings after sintering was determined using X-ray diffraction (XRD) analysis.

2.3. Oxidation tests on SiC fibre substrates

Thermogravimetric analysis (TGA-DTA) (Stanton Redcroft, STA-780) was carried out on as-received silicon carbide fibres. A slow heating rate (5°C/min) was used to allow measuring the changes of weight with increasing temperature up to 1200°C. The sample was kept for 1 h at 1200°C. The results of the TGA-DTA analysis were used to design the oxidation resistance tests. These were carried out in an electric furnace (Lenton Furnace, Ltd.) in normal atmosphere at 1000°C. Previously weighted titania coated and uncoated SiC fibrous substrates were placed simultaneously in the furnace. At pre-determined times (up to 120 h), coated and uncoated samples were removed and weighted in a 10^{-5} g precision balance.

2.4. Composite fabrication from TiO_2 coated carbon fibre substrates

For carbon fibre substrates, a second infiltration of EPD coated (and pre-sintered) fibre substrates was carried out by means of a simple slurry-dipping technique, with the aim to produce model 3-D titania matrix composite samples. Two different approaches were investigated. In the first method, TiO_2 nanoparticles in the as received condition were dispersed in distilled water in order to produce a slurry of 40 wt% solids loading. Then the EPD coated and presintered carbon fibre samples were dipped for 5, 10 and 15 min into the solution, dried in a constant humidity chamber at room temperature and subsequently sintered again at 800°C for 2 h in argon. In the second experimental approach, agglomerated titania particles were used. To prepare the particles, the solution used in the previous method was dried in an oven and the remaining powder was crushed in a mortar. This agglomerated powder was dispersed in water at a concentration of 40 wt%. In this slurry, the powder particles were agglomerated and the particle size was >1 μm. The same dipping times as well as drying and sintering conditions applied in the first approach were used. The microstructure of polished sections and fracture surfaces were observed by SEM.

3. Results

3.1. Production and characterisation of TiO_2 coatings

The EPD process under constant voltage conditions for both types of fibres followed a similar behaviour as that proposed by Sarkar and Nicholson [22], i.e., the electric current decreased continuously with deposition time due to the increase of the electric resistance as deposition progressed. It was possible to observe that TiO_2 nanopowder strongly adhered to the SiC and carbon fibre surfaces after the first minute of EPD for all voltages tested (30, 40 and 50 volts). For constant deposition time, the rate of deposition increased very quickly with voltage and it was difficult to control it at the higher voltages (40 and 50 volts). Thus, at these voltages it was difficult to avoid the growing of TiO_2 particle clusters on the fibres, which occurred specially in areas characterised by numerous fibre-fibre contacts. For an applied voltage of 30 volts, there was a higher number of well-coated fibres and the amount of drying cracks was lower than for 40 and 50 volts. Consequently, 30 volts was chosen as the optimal voltage for coating the carbon fibres. Similar observations were made on carbon fibre performs and 25 V was found to be the optimal deposition voltage. Fig. 1a and b are SEM micrographs of SiC

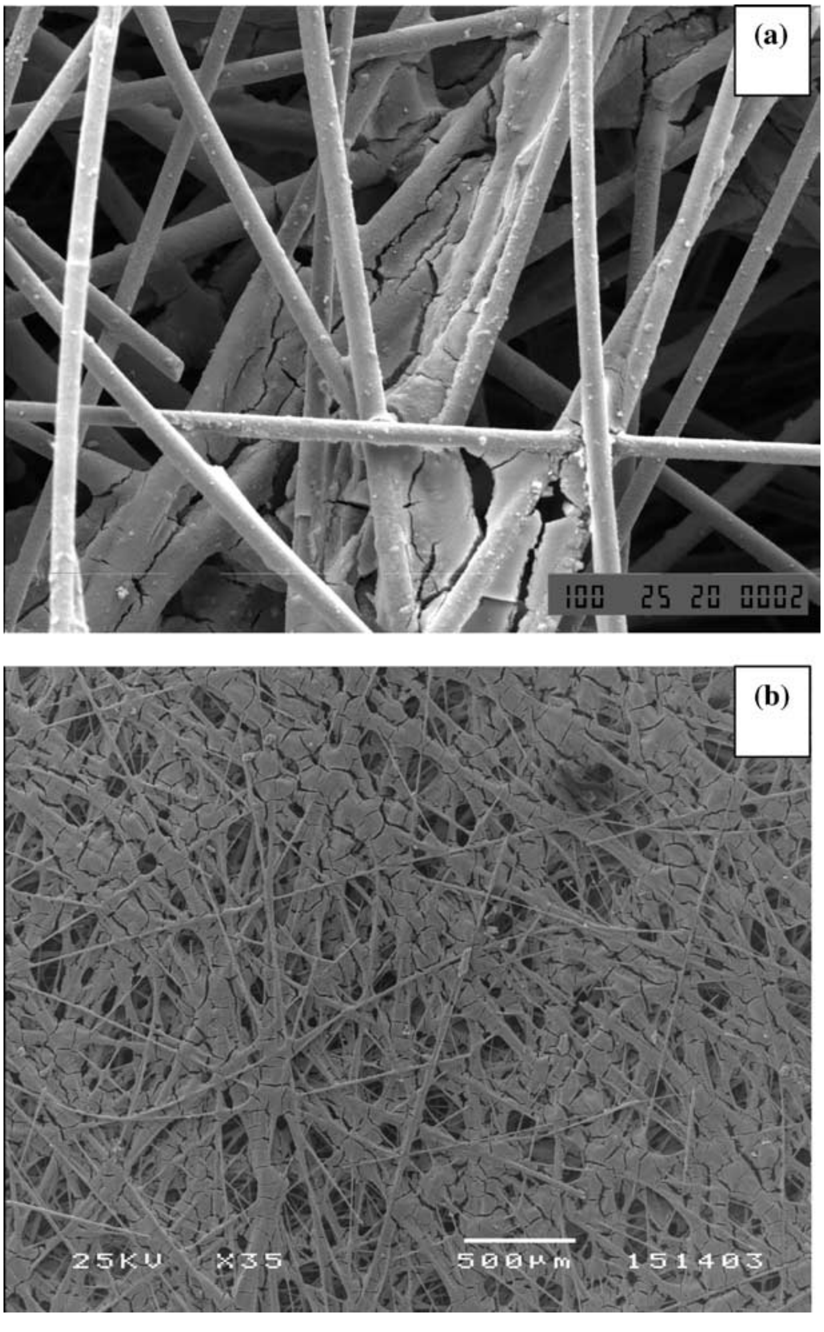

Figure 1 SEM micrographs showing fibres coated with TiO_2 by EPD after drying in a humid atmosphere: (a) SiC fibres (deposition voltage: 30 V) and (b) carbon fibres (deposition voltage: 25 V). The deposition time was 3 min in both cases.

and carbon fibre samples coated with TiO_2 nanoparticles for 3 min at 30 V and at 25 V, respectively. From microstructural SEM observations, three minutes was chosen as the optimum deposition time for experiments carried out at the optimised deposition voltage in both fibre types. This deposition time led to high-quality uniform coating on the individual fibres, minimizing the development of both microcracks and particle clusters (agglomeration) on all fibres throughout the sample. SEM observations also revealed that the more tightly spaced the fibres were, the higher the likelihood for production of TiO_2 particle clusters on them, as it can be appreciated in Fig. 1a and b. This may be due to the larger conductive surface offered by the sample during EPD, which should enhance the rate of deposition. These particle clusters or agglomerates are undesirable because they provide areas for easy development of microcracks during the drying process. Occurrence of microcracking upon drying is a common phenomenon in ceramic deposits produced by sol-gel and colloidal methods [28], and it is particularly problematic in thick deposits ($>5\ \mu$m) produced by EPD [6, 15, 25]. Microcracking development may be solved by applying a second EPD process to fill the open spaces with titania nanoparticles or by a more careful control-humidity drying process, i.e., inducing very slow drying rates.

Irrespective of the fibre substrate, the best sintering conditions for producing relatively dense and homogeneous coatings were found to be: sintering temperature: 800°C and dwelling time: 1 h. Fig. 2a and b show SEM images of TiO_2 coated SiC and carbon fibre substrates, respectively, sintered under these conditions. Both the extent of microcracking and residual porosity were minimized at 800°C sintering temperature. The

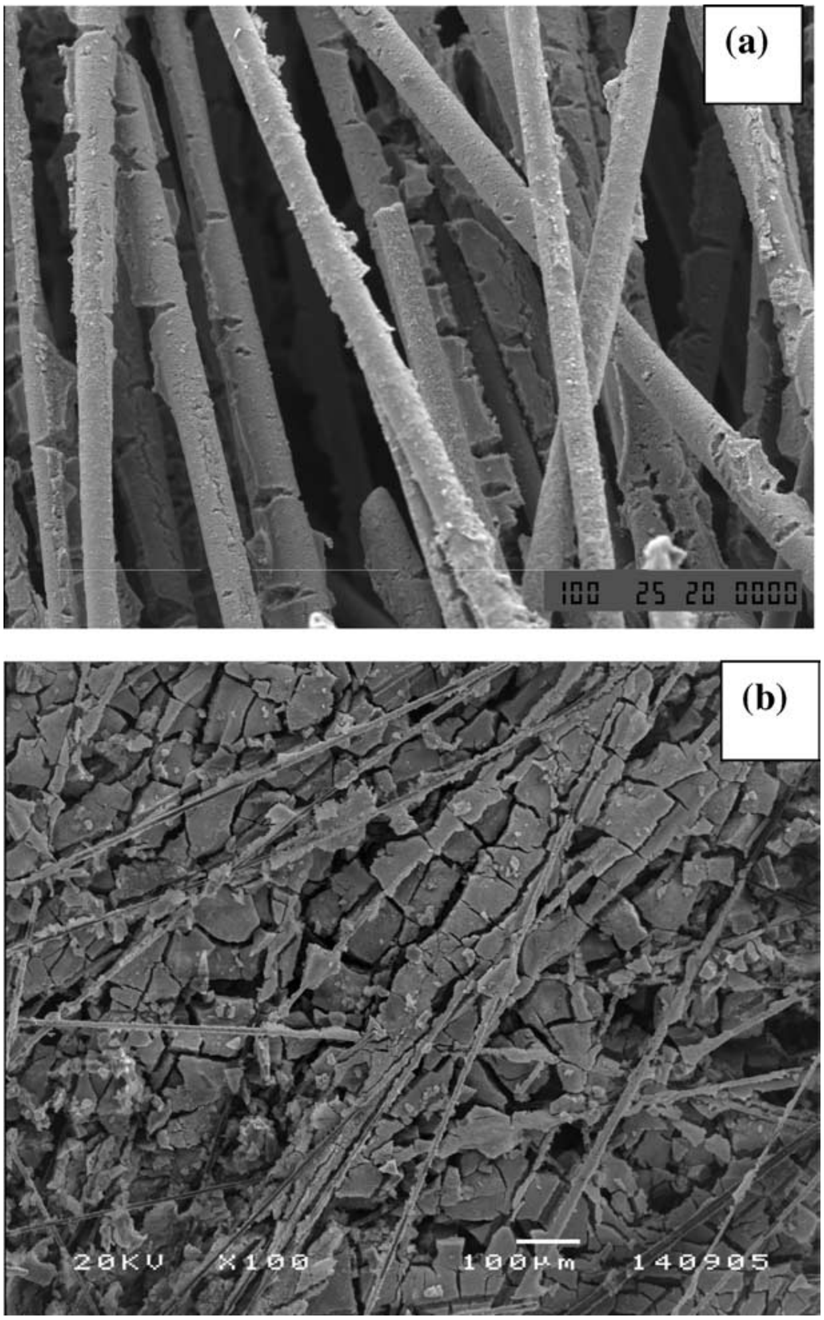

Figure 2 SEM micrographs of samples sintered at 800°C for 1 h, after EPD at the conditions given in Fig. 1: (a) SiC and (b) carbon fibres.

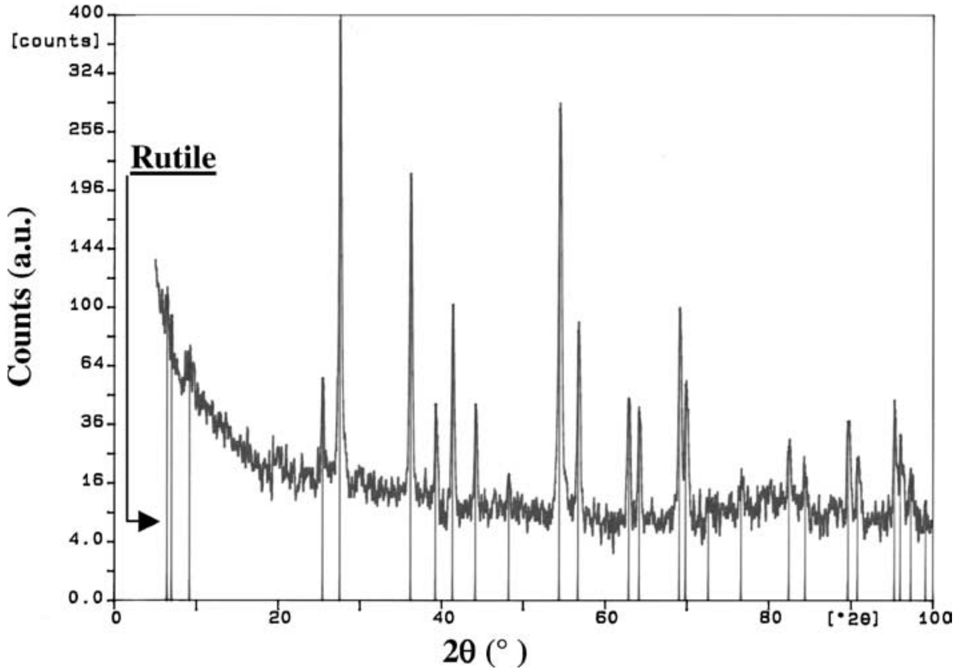

Figure 3 XRD pattern of the titania coatings on carbon fibres produced at 800°C showing the presence of rutile as the only crystalline phase.

crystalline structure of the coatings sintered at 800°C was determined by XRD, as shown in Fig. 3 for a sintered titania coating on carbon fibres. The crystalline pattern shows the presence of rutile as the only crystalline phase, indicating the transformation of anatase to rutile has occurred during the sintering process. Sintering at 1000°C did not show major improvement in the amount of porosity and it was observed that some cracks had become wider open. In fact, cracks developed during drying usually cannot be eliminated by the sintering process. On the contrary, microcracking development may be enhanced at higher sintering temperatures due to constrained shrinkage of the coating and also due to thermal stresses developed as consequence of the thermal expansion coefficient (α) mismatch between fibres (Nicalon® NL202, $\alpha = 3.1 \times 10^{-6}$/K or carbon, $\alpha = 0.3 \times 10^{-6}$/K [11]) and titania coating (rutile modification: $\alpha = 7.14 \times 10^{-6}$/K parallel, $\alpha = 9.19 \times 10^{-6}$/K perpendicular [29]).

High magnification SEM and FEG-SEM observations revealed in more detail the uniform microstructure of the sintered coatings, as shown in Fig. 4a and b, respectively, for a sintered titania coating on a carbon fibre. The coating thickness was calculated from SEM micrographs. It was observed that the coatings were composed of individual layer of 5 to 10 nanosized particles. This supposes a layer thickness of at least 0.105 μm for titania particles of 21 nm average diameter. This would indicate that the largest possible existing pore in the titania coating considering simple cubic arrangement of the grains, would be ~14.5 nm in diameter. Summarising this part of the study, it can be stated that the TiO_2 coatings produced by EPD covered well the surface of both the SiC and carbon fibres, with minimum amount of residual nanosized pores and low extent of microcracking. Coating was possible also in those regions with small fibre interspacing and fibre-fibre contact points, confirming the suitability of EPD to coat intricate porous fibrous structures with ceramic nanoparticles.

3.2. Oxidation tests on titania coated SiC fibres

DTA-TG tests on as-received SiC fibres in air indicated that significant oxidation of this fibre type starts at ~920°C. It is well known that when temperatures above 900°C are reached, a decrease in the mechanical properties of standard SiC Nicalon® fibres is observed [30], caused both by microstructure changes and oxidative degradation. In particular, the oxidation of SiC fibres in hot air leads to the formation of a SiO_2 crust formed by diffusion of oxygen on the surface of the SiC fibres [31]. The decrease in strength has been attributed to the formation of flaws, bubbles and cracks in the oxide film produced [30, 31].

In the present study, the oxidation of TiO_2 coated and uncoated Nicalon® fibre preforms was quantitatively assessed by considering the relative weight change occurred during exposure at 1000°C for up to 5 days. Fig. 5 summarizes the results of the oxidation test. The TiO_2 coated SiC fibres showed an increase of 0.99% in weight after having been exposed for 120 h at 1000°C, while the uncoated SiC fibres had an increase in weight of 3.30% for the same conditions.

Thermal degradation of the Nicalon® fibre involves the pyrolisis of the silicon-oxycarbide (Si_3C_4O) component to form CO and SiC with significant weight loss due to volatilisation. However, in the presence of oxygen, SiC is expected to react to form silica. The formation of silica contributes to weight gain. Thus during oxidation both mechanisms are active and consequently the weight measured is a resultant of the two competing processes. It has been shown however that the dominant mechanism is silica formation [32], and therefore a net weight gain during oxidation of Nicalon® fibres

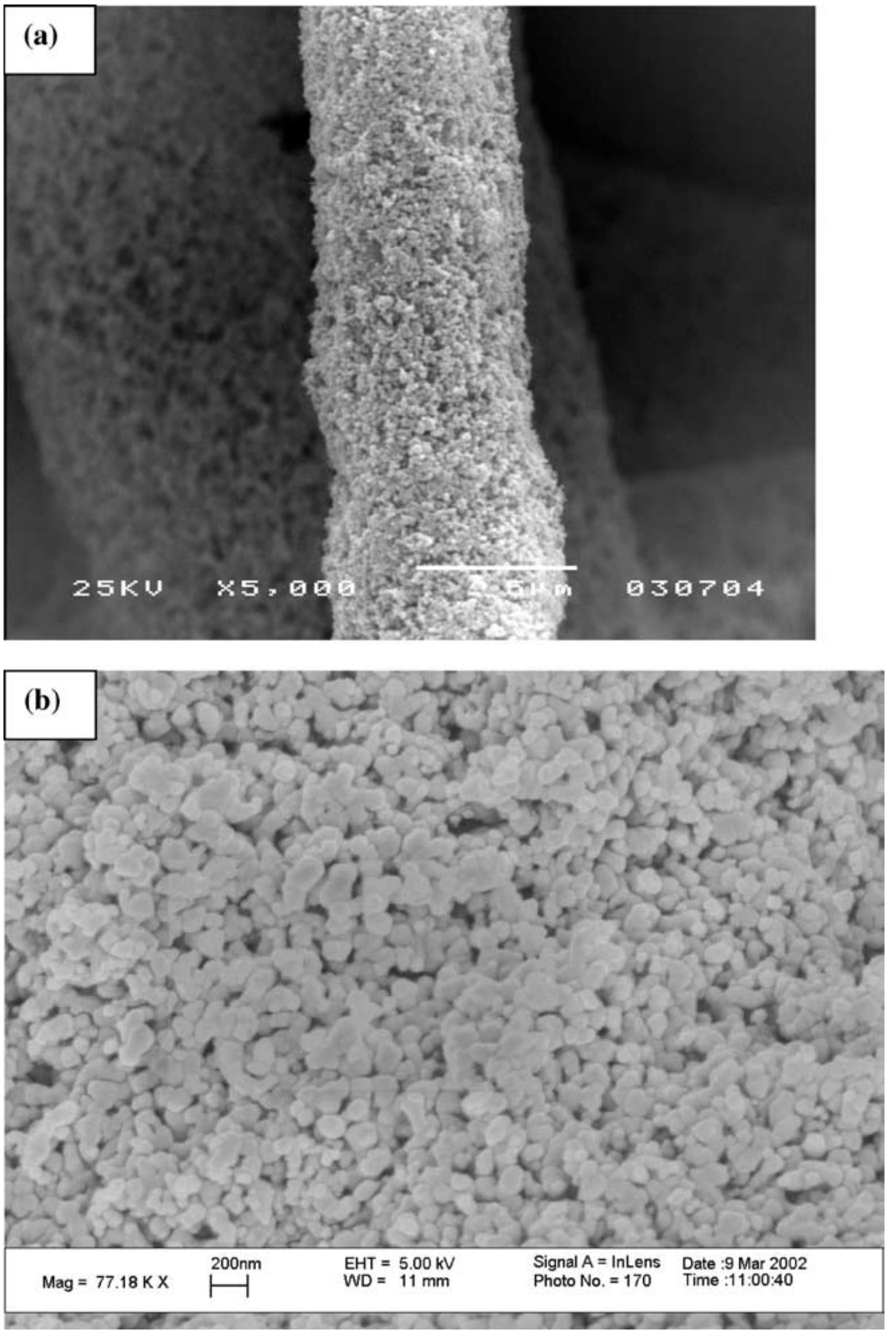

Figure 4 High magnification SEM (a) and FEG-SEM (b) micrographs of a TiO_2 coated carbon fibre sintered at 800°C for 1 h, showing uniform coating microstructure and low porosity in the nanoscale.

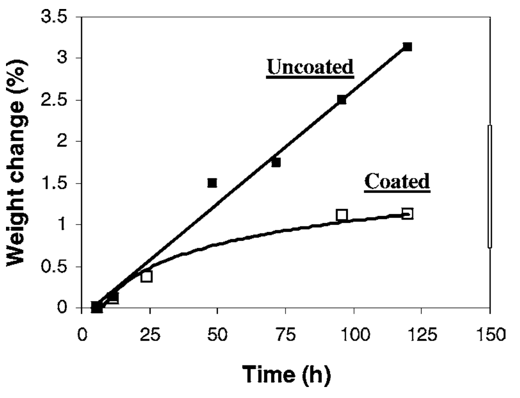

Figure 5 Results of the oxidation test carried out in air at 1000°C for TiO_2 coated and uncoated SiC fibres.

is expected, as found here. The results in Fig. 5 confirm that the coatings produced by EPD were effective in protecting the SiC fibres against oxidation in air at the conditions investigated. In addition, the oxidation of the SiC fibres followed a parabolic law, which is related to a process of diffusion as pointed out in the literature [33]. On the contrary, the titania coated fibres exhibited a lower rate of oxidation, which could be described empirically by a logarithmic law. Trend lines have been included in Fig. 5 to show the different time dependence of the oxidative behaviour of the coated and uncoated SiC fibres.

Fig. 6 is a SEM micrograph of an uncoated SiC fibre sample aged for 120 h at 1000°C, showing the aspect of the surface of the fibres. Some round grains have

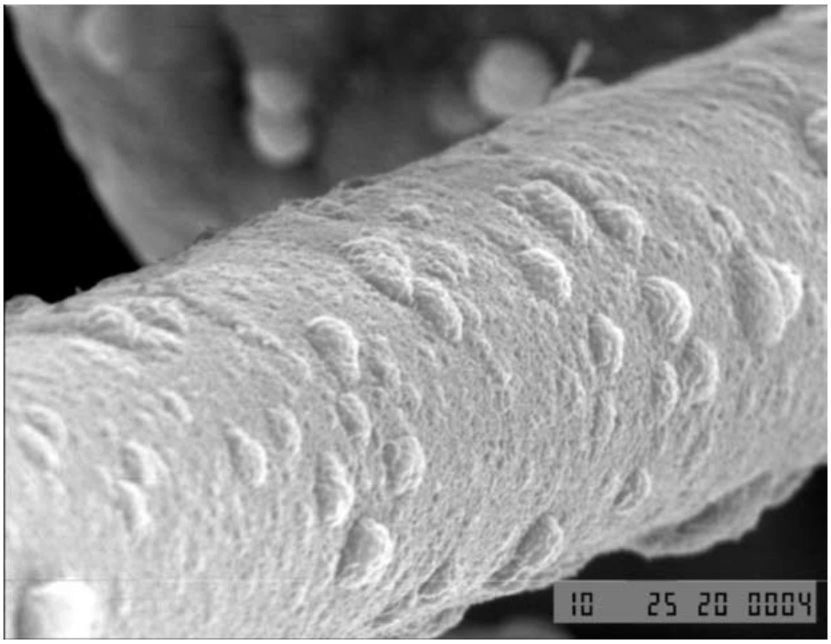

Figure 6 SEM micrograph showing an uncoated SiC fibre thermally aged for 120 h at 1000°C.

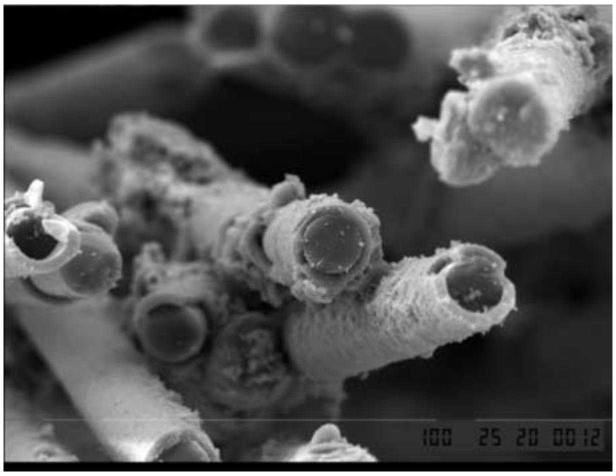

Figure 7 SEM micrograph showing titania coated SiC fibres thermally aged for 120 h at 1000°C.

grown and developed on all fibre surfaces, which is an indication of silica scale formation. This scale was crystalline cristobalite, as confirmed by XRD analysis (not shown here). Bubbles and flaws are also visible in Fig. 6. These findings indirectly confirm the formation of SiO_2 on the fibres, as the bubbles may be attributed to SiO and CO gas entrapment due to a poor diffusion of gases through SiO_2. Some fibres exhibited also some spallation on their surfaces, which may be attributed to the SiO_2 scale, which is poorly adhered to the surface of the fibres. A SEM micrograph corresponding to titania coated SiC fibres after aging for 120 h at 1000°C is shown in Fig. 7, indicating the stability of the titania coatings at the conditions investigated. The aspect of the titania coating also confirms that some further sintering of the coating has occured during the heat-treatment. Fig. 8 shows the surface of a SiC fibre once

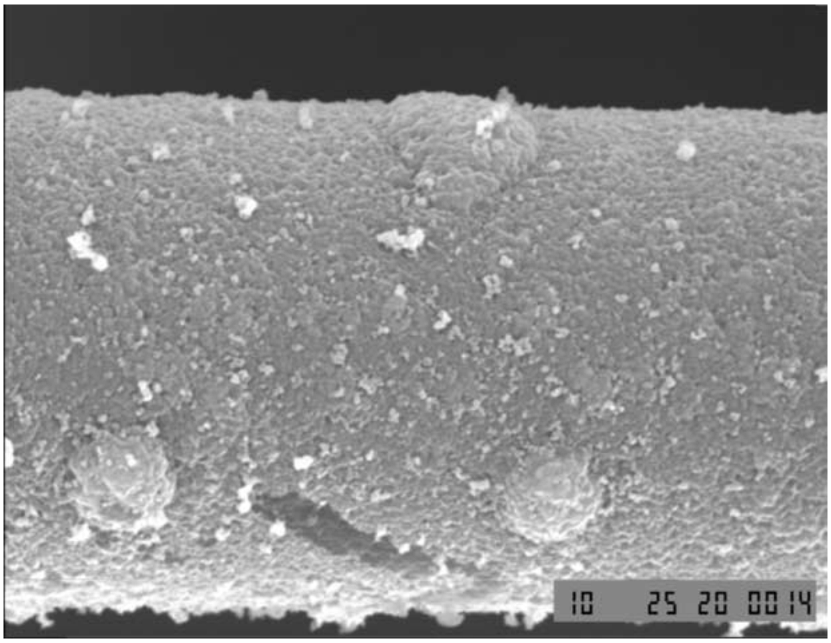

Figure 8 SEM micrograph showing the surface of a SiC fibre where the TiO_2 coating has been scratched away after aging for 120 h at 1000°C.

the TiO_2 coating has been scratched away from the fibre surface after the aging treatment (1000°C, 120 h), thus, this image reveals the condition of the surface of the SiC fibre beneath the TiO_2 coating. No degradation is observed apart from some pores that appeared in less proportion than for the uncoated fibre (see Fig. 6). The general aspect of the fibre surface indicates that it has not been too much affected by the thermal aging, qualitatively confirming the suitability of the titania coating as oxidation protection for the conditions investigated here. A further investigation is in progress, aiming at measuring the mechanical strength of individual TiO_2 coated SiC fibres before and after long term exposure to hot air.

3.3. Fabrication of 3-D carbon fibre reinforced TiO_2 matrix composites

The best results in terms of degree of titania particle infiltration into EPD coated carbon fibre preforms was achieved when the original nanosized TiO_2 powder was used to prepare the slurry. Therefore only results achieved using this method will be presented and discussed here. The optimal slurry coating time was 15 min. The typical microstructure of EPD coated and slurry infiltrated 3-D carbon fibre titania matrix composites after sintering for 2 h at 800°C is shown in Fig. 9a, while Fig. 9b is an SEM image of the fracture surface of such a composite. Both images demonstrate a high level of ceramic infiltration into the porous fibrous

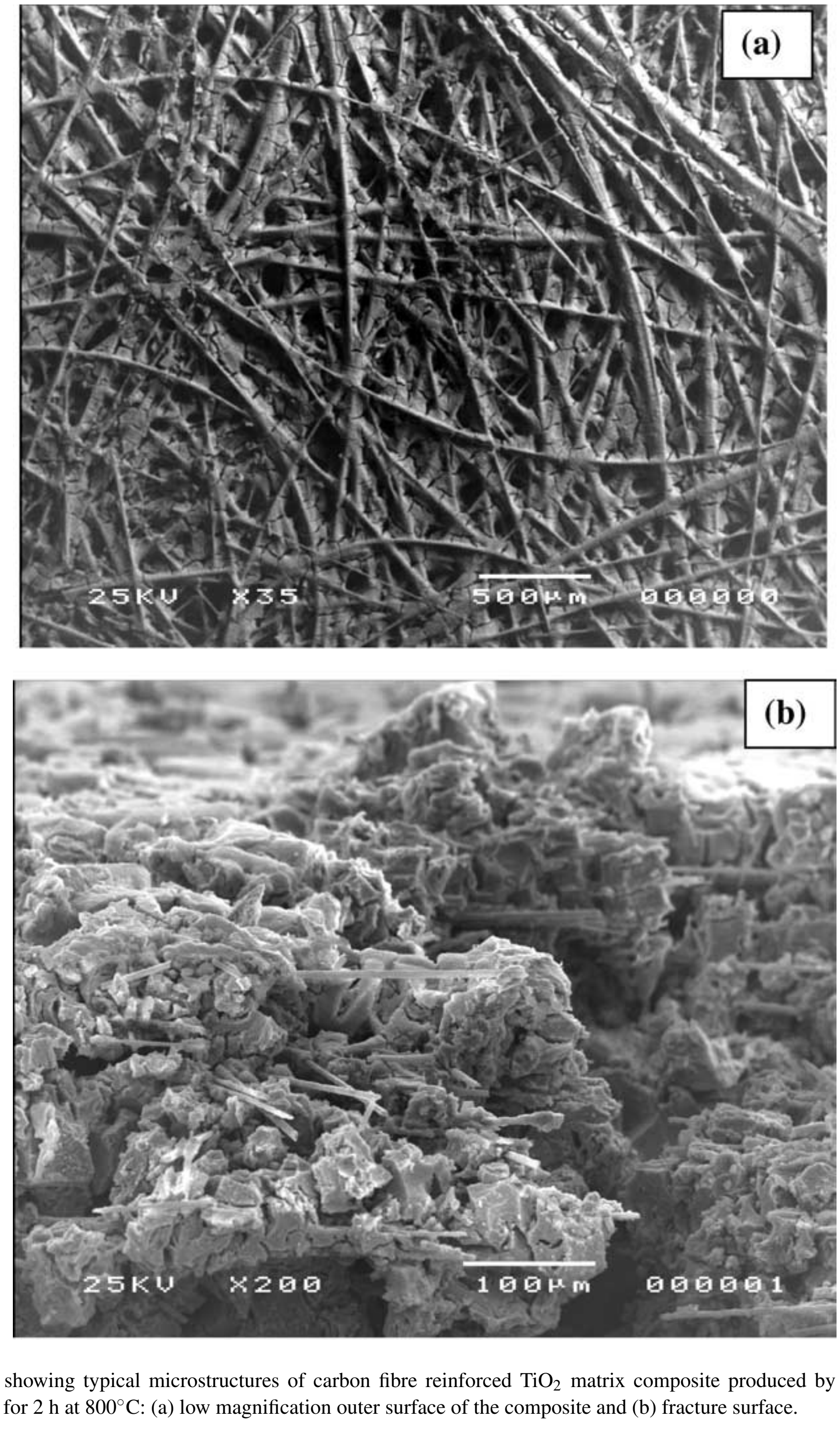

Figure 9 SEM images showing typical microstructures of carbon fibre reinforced TiO_2 matrix composite produced by EPD, subsequent slurry infiltration and sintered for 2 h at 800°C: (a) low magnification outer surface of the composite and (b) fracture surface.

structure, however some residual porosity, mainly between fibre tows, is still present. The mechanical properties of the 3-D TiO_2/carbon fibre composites were not measured because only small rectangular samples were produced in the framework of this investigation. In spite of the residual porosity, it was found that, qualitatively, the samples exhibited sufficient structural integrity and high fracture resistance when they were manually fractured by impact using a hammer. Current research focuses on testing the mechanical properties of the samples.

4. Conclusions

High-quality, uniform and reproducible TiO_2 coatings on 3-D SiC and carbon fibre preforms were produced by EPD using non-aqueous suspensions of titania nanoparticles and constant voltage conditions. A very short deposition time (3 min) was sufficient to achieve a high-quality coating microstructure. These TiO_2 coatings were smooth and completely covered the surface of the SiC and carbon fibres throughout the thickness of the fibrous substrates (3 mm). The development of microcracks on the surface of the coatings, which tended to occur during the drying process after EPD, was minimized by using low-rate drying of the samples in humid atmosphere. Sintering at 800°C for 1 h in argon environment produced strong adherence of the nanosized titania particles to the surface of the fibres. The TiO_2 coatings were tested for up to 120 h at 1000°C for oxidation protection of the SiC fibres. It was found that TiO_2 coating stopped the increase of weight due to oxidation of the fibres after 72 h and that the rate of oxidation was much lower than that of bare SiC fibres. The fabrication of 3-D carbon fibre reinforced titania matrix composites using the EPD coated carbon fibre preforms was attempted. A post-EPD infiltration of the fibrous substrates by slurry dipping using TiO_2 nanoparticles in aqueous suspensions was carried out. After sintering at 800°C for 2 h the samples exhibited (qualitatively assessed) adequate structural integrity despite the residual porosity present. Current developments are focused on improving the density of the composites and on measuring their mechanical properties.

Acknowledgements

ARB acknowledges financial support of the Nuffield Foundation, London (Grant Nr. NAL/00196/G).

References

1. K. VYDIANATHAN, G. NUESCA, G. PETERSON, E. T. EISENBRAUN and A. E. KALOYEROS, *J. Mater. Res.* **16** (2001) 1838.
2. E. SZALKOWSKA, J. GLUSZEK, J. MASALSKI and W. TYLUS, *J. Mater. Sci. Lett.* **20** (2001) 495.
3. M. BUCHMANN, R. GADOW and D. SCHERER, *Ceram. Eng. Sci. Proc.* **23**(4) (2002) 103.
4. J. P. CLEMENT, H. J. RACK, K. T. WU and H. G. SPENCER, *Mater. Manuf. Processes* **51** (1990) 17.
5. T. HASHISHIN, J. MURASHITA, A. JOYAMA and Y. KANEKO, *J. Ceram. Soc. Jpn.* **106** (1998) 1.
6. A. R.BOCCACCINI, U. SCHINDLER and H.-G. KRUEGER, *Mater. Lett.* **51** (2001) 225.
7. R. SAKAMOTO, H. NISHIMORI, M. TATSUMISAGO and T. MINAMI, *J. Ceram. Soc. Jpn.* **106** (1998) 1034.
8. S. R. DHAKATE, V. K. PARASHAR, V. RAMAN and O. P. BAHL, *J. Mater. Sci. Lett.* **19** (2000) 699.
9. R. L. DONG, H. SUEYOSHI, M. HIGO, Y. UEMURA and Y. HIRATA, *J. Ceram. Processing Res.* **2** (2001) 72.
10. M. K. CINIBULK, *Ceram. Eng. Sci. Proc.* **17**(4) (1996) 241.
11. R. WURM, O. DERNOVSEK and P. GREIL, *J. Mater. Sci.* **34** (1999) 4031.
12. H. LI, J. LEE, M. R. LIBERA, W. Y. LEE, A. KEBBEDE, M. J. LANCE, H. WANG and G. N. MORSCHER, *J. Amer. Ceram. Soc.* **85** (2002) 1561.
13. M. VERDENELLI, S. PAROLA, F. CHASSAGNEUX, J.-M. LETOFFE, H. VINCENT, J.-P. SCHARFF and J. BOUIX, *J. Europ. Ceram. Soc.* **23** (2003) 1207.
14. D. B. GUNDEL, P. J. TAILOR and F. E. WAWNER, *J. Mater. Sci.* **29** (1994) 1795.
15. A. R. BOCCACCINI and C. B. PONTON, *JOM* **47**(7) (1995) 34.
16. P. A. TRUSTY, C. B. PONTON and A. R. BOCCACCINI, *Ceram. Trans.* **83** (1998) 391.
17. A. R. BOCCACCINI, C. KAYA and K. K. CHAWLA, *Composites: Part* A **32** (2001) 997.
18. I. ZHITOMIRSKY, *J. Europ. Ceram. Soc.* **18** (1998) 849.
19. *Idem.*, *Mater. Lett.* **38** (1999) 10.
20. C. KAYA, A. R. BOCCACCINI and K. K. CHAWLA, *J. Amer. Ceram. Soc.* **83** (2000) 1885.
21. B. SU, C. B. PONTON and T. W. BUTTON, *J. Europ. Ceram. Soc.* **21** (2001) 1539.
22. SARKAR and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **79** (1996) 1987.
23. A. R. BOCCACCINI and I. ZHITOMIRSKY, *Curr. Opin. Solid State Mater. Sci.* **6** (2002) 251.
24. O. VAN DER BIEST and L. VANDEPERRE, *Ann. Rev. Mater. Sci.* **29** (1999) 327.
25. E. R. KREIDLER and V. P. BHALLAMUNDI, *J. Ceram. Process. Res.* **2** (2001) 93.
26. "Technical Bulletin Pigments," No. 56, 6th ed. (Degussa AG, Frankfurt, Germany, 1993).
27. S. OKAMURA, T. TSUKAMOTO and N. KOURA, *Jpn. J. Appl. Phys.* **32** (1993) 4182.
28. C. J. BRINKER and G. W. SCHERER, "Sol-Gel Science" (Academic Press, New York, 1990).
29. http://www.mt-berlin.com/charts/chart_07.htm#IND10, acceded 29/5/2002.
30. K. K. CHAWLA, "Fibrous Materials" (Cambridge University Press, Cambridge, 1998).
31. R. GADOW and K. VON NIESSEN, *Ceram. Eng. Sci. Proc.* **23**(3) (2002) 277.
32. T. ISHIKAWA, *Comp. Sci. Technol.* **51** (1994) 135.
33. M. HUGER, S. SOUCHARD and D. GAUL, *J. Mater. Sci.* **12** (1993) 414.

Received 20 April
and accepted 28 July 2003