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Fabrication of CNT-SiC/SiC composites by electrophoretic deposition

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Abstract

Due to the outstanding mechanical and thermal properties of carbon nanotubes (CNTs), they are considered suitable reinforcement for structural materials. In this study, for the first time, electrophoretic deposition (EPD) was used to deposit (multi-walled) CNTs onto SiC fibres (SiC_f) to form an effective CNT interphase layer for SiC_f/SiC composites. This deposition was followed by electrophoretic infiltration of the CNT-coated SiC fibre mats with SiC powder to fabricate a new CNT-SiC-fibre-reinforced SiC-matrix (SiC_f/SiC) composite for fusion applications. In these EPD experiments, a commercial aqueous suspension of negatively charged CNTs and an optimized aqueous suspension of negatively charged SiC particles were used. The CNT-coatings on the SiC fibres were firm and homogenous, and uniformly distributed nanotubes were observed on the fibre surfaces. In a following step of EPD, a thick SiC layer was formed on the fibre mat when the CNT-coated SiC fibres were in contact with the positive electrode of the EPD cell; however, spaces between the fibres were not fully filled with SiC. Conversely, when CNT-coated SiC fibres were isolated from the electrode, the SiC particles were able to gradually fill the fibre mat resulting in relatively high infiltration, which leads to dense composites.

Keywords: Electrophoretic deposition; SiC_f/SiC composite; Carbon nanotubes (CNTs); Coatings; Interphase

1. Introduction

Continuous SiC-fibre-reinforced SiC composites have been recognized as promising materials for use in the structural parts of future fusion reactors due to the high thermal stability of SiC offering the possibility of high temperature operation of the reactor and hence more economic energy production.[1] In addition, due to the low neutron activation of pure SiC, these composites represent a way to minimise the amount of radioactive waste generated during reactor operation in comparison with ferrous materials. To ensure sufficient fracture toughness and reliability of the material, SiC is proposed to be used in the form of continuous SiC-fibre-reinforced SiC ceramics, i.e., a (SiC_f/SiC) composite.[1–3] The composite is composed of SiC fibres woven in a 2D or 3D architecture, filled with a matrix material that is either pure SiC produced by chemical vapour infiltration or by infiltration of a polymer precursor, or with a particulate composite of a liquid phase sintered SiC. The fibres are coated with an interphase layer, typically pyrolitic carbon of 100–500 nm that is usually deposited by a chemical vapour deposition (CVD) process, and has the main task to protect the material from catastrophic fracture by deflecting the propagating crack and inducing fibre pull-out, which is the most efficient toughening mechanism in this class of composites.[4]

However, no state-of-the-art material meets all of the highly demanding requirements for use in fusion reactors. The ceramic composites, for example, are associated with several still unresolved issues, including gas permeability, insufficient mechanical properties at high temperature, too high neutron activation, too low thermal conductivity, and instability of the fibres at high temperatures. The thermal conductivity and the mechanical properties of a composite are highly dependent on the chemical composition of its three constituents (the matrix material, the fibres, and the interphase layer), and on its porosity.

Among the strategies to improve the overall performance of SiC_f/SiC composites, in particular to increase their mechanical strength and thermal conductivity, incorporation of carbon nanotubes (CNTs) is highly promising, due to their outstanding mechanical and thermal properties. The CNTs are characterised not only by a very high thermal conductivity (>2000 W/mK)[5–7] and ability to increase the toughness of intrinsically brittle

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materials, probably through "bridging" and "pull-out" toughening mechanisms,[8–11] but also by a relatively high thermal stability in non-oxidising atmospheres. The potential benefit of CNTs in ceramic matrix composites which arises from their tubular three-dimensional structure, has prompted significant research in the field, with CNTs and CNT-reinforced materials being among the most studied materials within the last decade.[12] The results from these studies strengthen the belief that CNTs will enable a breakthrough in the development of high-performance structural materials.[13]

Carbon nanotubes have been incorporated into many different inorganic matrices, ranging from glass and bioactive glass–ceramic[14–18] to various polycrystalline engineering ceramics (e.g., Al_2O_3, $BaTiO_3$, TiN, Si_3N_4, SiC).[19–25] There are also a few reports on CNTs grown on ceramic fibres;[26–29] however, due to a lack of quantitative data available no firm conclusion can be drawn about the property improvement achieved by the in situ synthesised CNTs. Since the as-prepared CNTs are intrinsically inert and uncharged, it is known that they are difficult to disperse in liquids. Acid treatment and use of specific surfactants enable a relatively good dispersion based on a certain surface charge. This in turn enables processing in an electric field to form deposits on different substrates.[31–33] Recent papers also report on composite deposits fabricated by co-deposition or subsequent deposition of CNTs with different ceramic powders (e.g., SiO_2, Fe_3O_4, TiO_2, and HA).[34–38]

To the best knowledge of the authors, the use of EPD to coat SiC fibre mats with CNTs has however never been reported; CNTs have been electrophoretically deposited on ITO glass, graphite and metallic substrates, as reviewed elsewhere[30] and on carbon fibre paper.[39] In this study, we report on the electrophoretic deposition of CNTs onto SiC fibre mats, thereby forming a continuous interphase layer on the fibres, followed by an infiltration of the coated-fibre mat with SiC powder, which forms a new CNT-SiC_f/SiC grade of fusion-relevant composite material.

2. Experimental

An aqueous suspension of multi-walled carbon nanotubes (Aquacyl), with average diameter 9.5 nm and average length 1.5 μm, was provided by Nanocyl S.A. (Sambreville, Belgium). The solids content in the as-received suspension was 1 wt.%. In this study, we used a SiC powder with an average grain size of 0.5 μm (SiC BF12, H. Starck, Germany). The zeta-potential (ZP) of the SiC powder and of the CNTs was measured in undiluted suspensions using a ZetaProbe analyser (Colloidal Dynamics, USA). A ZetaPals instrument (Brookhaven, USA) was used to analyse the ZP of the crushed SiC fibres in diluted aqueous suspensions. The pH levels were adjusted using 1 M sodium hydroxide (NaOH) and 1 M hydrochloric acid (HCl). The surface charge of the SiC particles for EPD was modified with tetramethyl-ammonium hydroxide (TMAH, Sigma–Aldrich), whereas the commercial CNT-suspension already contained anionic surfactant. The suspensions were homogenised using a strong probe-type ultrasound (Hielscher Ultrasonics, Germany), before the ZP measurement and EPD.

The EPD experiments were performed with (1) aqueous suspensions containing 0.0625–0.5 wt.% of carbon nanotubes at a constant dc voltage of 2.8 V for 10 or 20 min, and/or (2) suspensions containing 60 wt.% of SiC powder at a constant dc voltage of 30 V for 5 min. Electrodes made of steel, copper (both of dimensions: 20 mm × 10 mm × 0.2 mm), or graphite (20 mm × 5 mm × 2 mm) were vertically immersed in the suspension in the EPD cell. The distance between electrodes was 2 cm. In the CNT- and SiC-coating processes, the SiC-fibre mat (Tyrano SA, Ube Industries, Ltd., Japan) was placed in front of the electrode, whereas for the SiC-infiltration, the SiC fibre mat was electrically insulated from the electrode with a Teflon® spacer, as described elsewhere.[40] Before deposition, the electrodes were thoroughly cleaned in acetone using an ultrasonic treatment, washed with distilled water, and dried with compressed air. The SiC fabric was pre-treated with a sodium dioctyl-sulfosuccinate (SDOSS) solution to improve wettability.[41] After the deposition, the samples were dried in air at room temperature, vacuum-infiltrated by an aluminium dihydrogen phosphate ($Al(H_2PO_4)_3$) aqueous solution (TKI Hrastnik, Slovenia), and sintered at 1300 °C in argon (Ar) for 3 h. The microstructures of the green and sintered samples were observed using field emission gun scanning electron microscopes (FEG-SEM, LEO 1525, and Zeiss SUPRA 35VP). The sintered samples were inspected by EDS.

3. Results and discussion

The scanning electron micrograph in Fig. 1 shows the morphology of the carbon nanotubes used in this study. The carbon nanotubes have a high aspect ratio and a random and curled structure, which is typically associated with CNTs produced by thermal chemical vapour deposition (CVD).[9]

3.1. Electrokinetic properties of SiC fibres and characteristics of suspensions

Before performing the EPD experiments, we analysed the electrokinetic properties of the SiC powder and the CNTs suspensions (with solids contents of 25 and 1 wt.%, respectively).

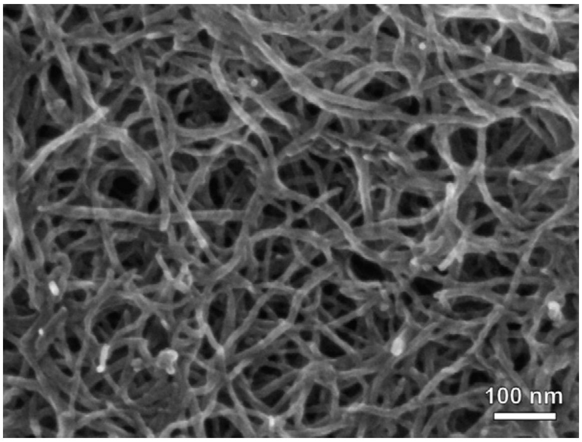

Fig. 1. SEM micrograph of the used CNTs.

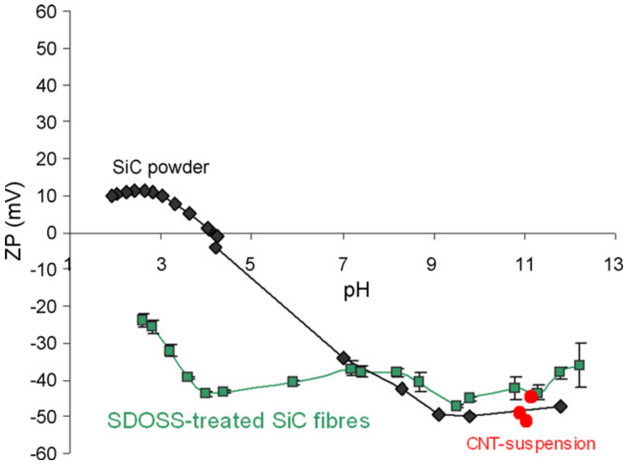

Fig. 2. Zeta-potential vs. pH of the materials investigated.

Since an appropriate net surface charge of fibres is very important for efficient electrophoretic infiltration,[42] we also analysed the ZP of crushed SiC fibres. The ZP vs. pH relationship is presented in Fig. 2. The as-received CNT-suspension is alkaline (pH 11), and due to the presence of anionic surfactant, the CNTs are negatively charged (ZP = −45 mV). The natural pH (pH 4) of the as-received SiC-powder suspension nearly matches the isoelectric point, resulting in a very unstable suspension. Titration with hydrochloric acid is not efficient at increasing the zeta-potential (described elsewhere[42]); conversely, titration of the SiC suspension with an appropriate amount of NaOH or TMAH increases the negative ZP up to −50 mV at a pH value of 10.

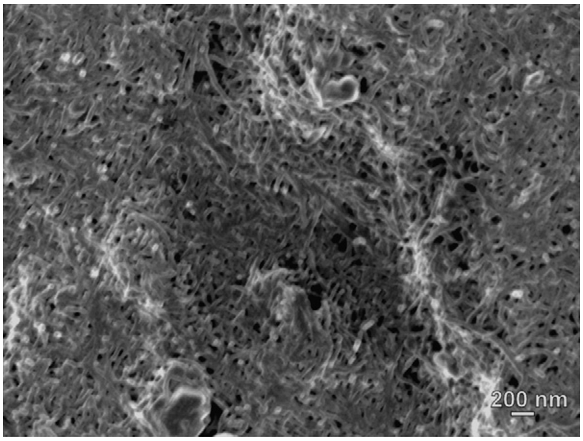

Fig. 3. SEM image of a CNT-coating made on a graphite electrode by EPD (2.8 V, 5 min).

In addition to the appropriate surface charge of the fibres, good wettability by the suspension is also an important characteristic for the infiltration of the fibre mats. Consequently, we decreased the natural wetting angle of the alkaline aqueous suspension at the SiC fibre bundle (∼80°) by pre-treating the fibres with the surfactant SDOSS, to approximately 30°. As shown in Fig. 2, the zeta-potential of the SDOSS-treated SiC fibres is negative over a wide range of alkaline pH values. Hence, as presented, the pre-treated SiC fibres, the SiC powder, and the CNTs are characterised with a relatively high negative zeta-potential in the alkaline pH region.

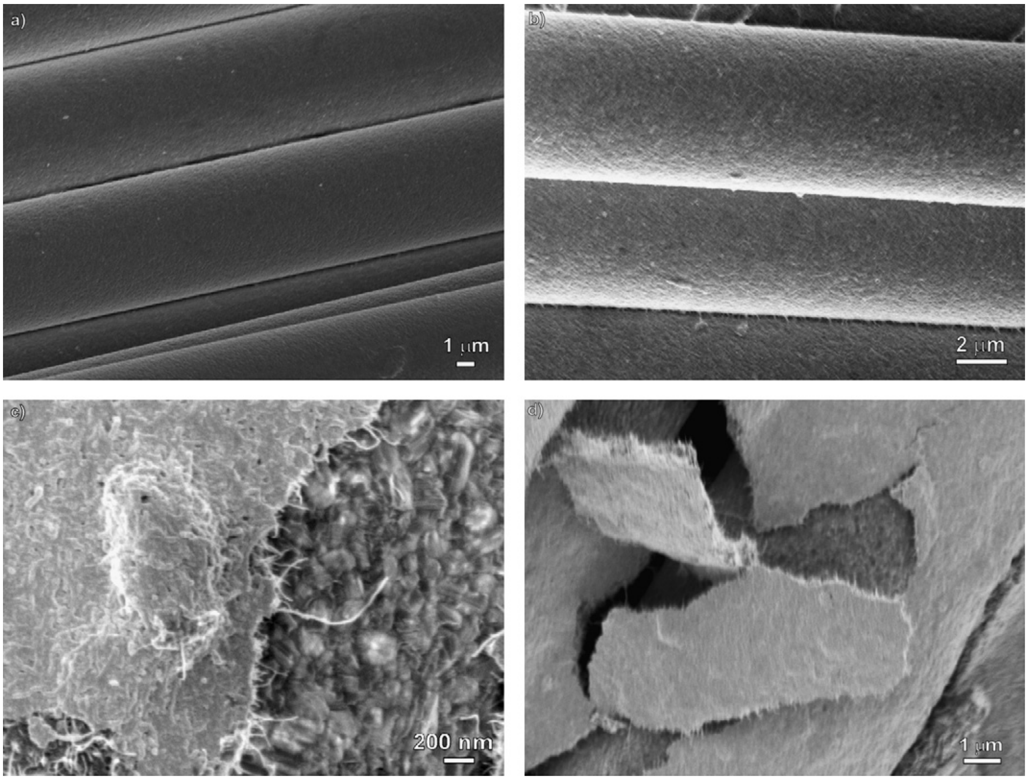

Fig. 4. SEM micrographs of (a) non-coated, (b–d) coated SiC fibres with carbon nanotubes at different magnifications.

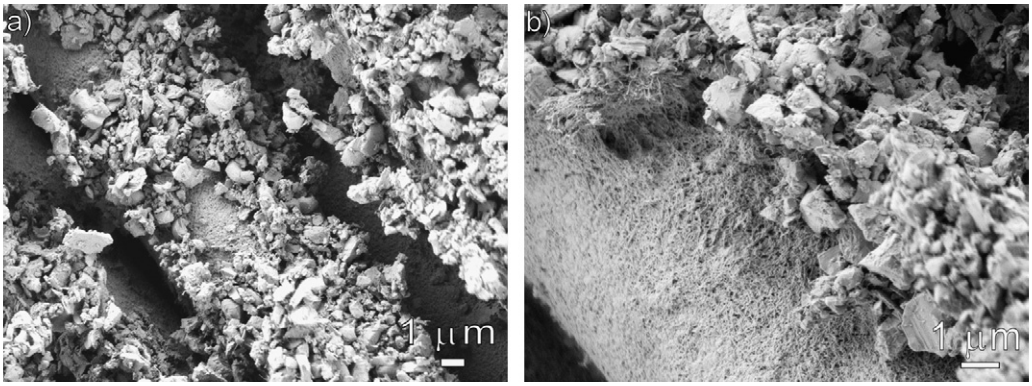

Fig. 5. (a and b) SEM micrograph of the fracture surface of a CNT-coated SiC fibre after SiC deposition by electrophoresis at two different magnifications.

3.2. Electrophoretic deposition of carbon nanotubes on metallic electrodes and SiC-fibres

The EPD experiments were first performed using a CNT-suspension with a solids content of 0.5 wt.%, on steel, copper, or graphite electrodes. Due to the negative ZP of CNTs in suspension, the deposits were always formed on the anode. Initially we performed an EPD experiment on a steel electrode. At voltages higher than 2.8 V, the electrolysis of water apparently limited the deposition, whereas at lower voltages, no deposit of carbon nanotubes was observed after 10 min. With a copper electrode, the bubble formation was suppressed due to the oxidation of copper. A solid CNT-coating was also formed on a graphite anode at 2.8 V in 5 min. From the higher magnification image in Fig. 3, it is evident that the CNTs form a fairly uniform coating and that they are evenly distributed on the graphite electrode.

In further EPD experiments, the SiC fibre mats were attached to the front side of the anode and were coated with a layer of CNTs at an applied voltage of 2.8 V for 10 min. In these experiments, the SiC fabric was in contact with the anode so that it acted itself as the electrode. A similar result could be obtained by using the fibre mat directly as an electrode, as shown elsewhere on the SiC/mullite system,[43] however, due to the lower conductivity of the SiC fibres compared with a metal electrode,

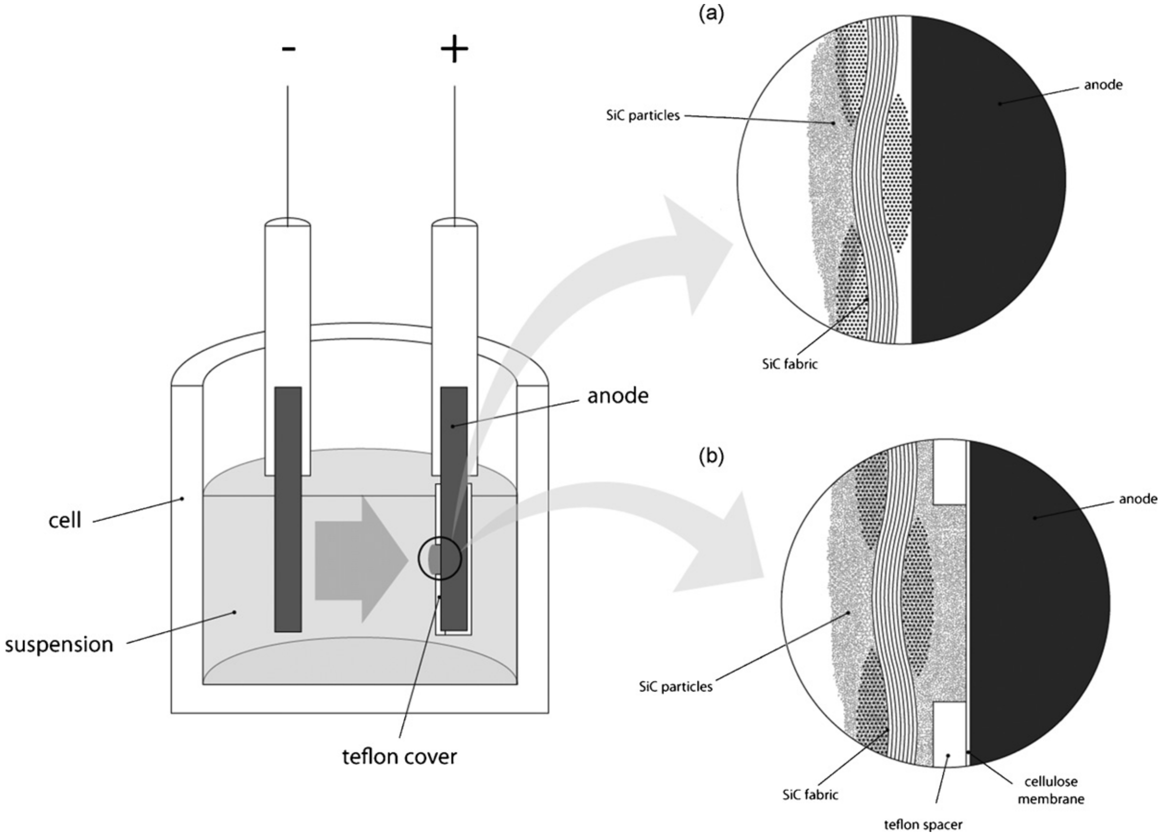

Fig. 6. Schematic representation of the EPD cell used for infiltration of SiC fibre fabric with SiC particles: (a) SiC-fabric is in contact with the electrode and (b) SiC-fabric is not in contact with the electrode.

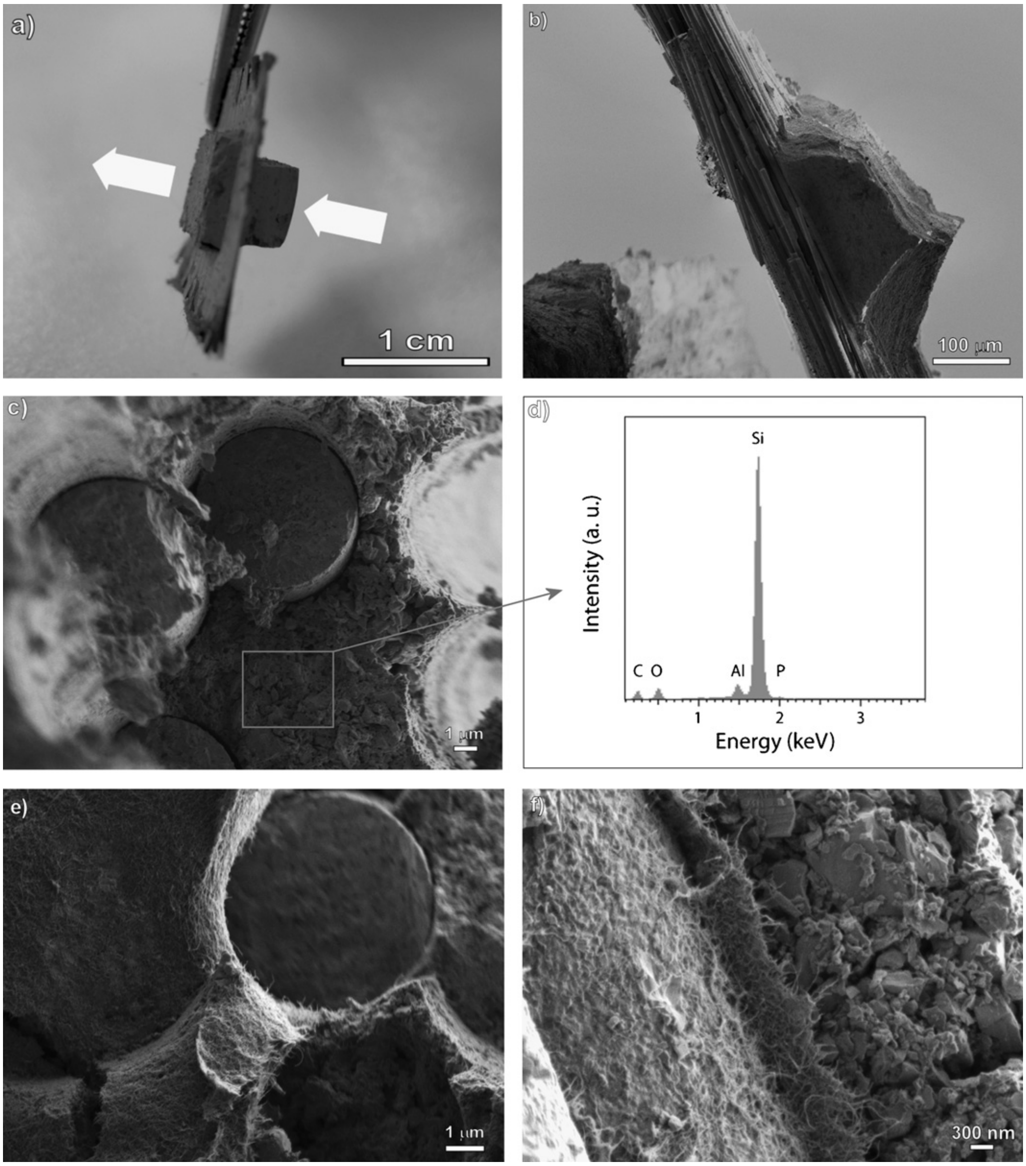

Fig. 7. (a) Macroscopic view of a green SiC fibre fabric, which was first coated with CNTs and then infiltrated with a SiC particle suspension by electrophoresis; (b, c, e) and (f) SEM micrographs of the sintered part (1300 °C in Ar) at different magnifications and different zones in the central part of the composite; (d) EDS spectrum of the matrix between the CNT-coated SiC fibres.

the applied voltage needs to be higher to achieve the same effect. Another reason for using the solid rectangular electrode in this study is that it results in a more homogenous electric field. SEM micrographs in Fig. 4a and b show the SiC fibres before and after deposition with the CNTs, respectively. From Fig. 4b it is evident that the fibres are completely covered with a thin layer of CNTs. The high-magnification SEM micrographs in Fig. 4c and d show a fairly uniform layer of CNTs (estimated thickness up to 400 nm) on the SiC fibre. Due to their very small size and well-dispersed state, the carbon nanotubes were able to penetrate into the spaces between the fibres in the 2D fabric. By observing the cross-section of the sample we confirmed that the SiC-fibres in the central region of the fibre mat were also efficiently coated by the CNTs. This can be clearly seen in Fig. 7e and f, which show CNT-coated fibres inside the central region of the sintered CNT-SiC/SiC composite.

3.3. Electrophoretic infiltration of CNT-coated SiC fibre mats with SiC particle suspension

In the next step, we electrophoretically infiltrated the CNT-coated fibre mat with a suspension of SiC powder. As reported elsewhere,[40–42,44] SiC powder can be deposited either from ethanol or water. However, higher ZP values can be obtained in aqueous suspensions, resulting in deposits with higher particle packing density. In the present investigation, we deposited SiC particles onto the SiC fibres from a suspension containing 60 wt.% solids and including TMAH, at 30 V for 5 min. In the first EPD trials, the CNT-coated fibre mat was placed in front of the anode so that it was in direct contact with the electrode. This caused deposition of the negative SiC particles onto the SiC fibres, which acted as the anode. As expected, the SiC particles formed a firm deposit on the CNT-coated SiC fibres. Fig. 5a and b illustrates the fracture surface of the CNT-coated silicon carbide fibre tow after the deposition with SiC. It is clear that the uniformly distributed nanotubes on the SiC fibres are coated by SiC particles, while the gaps between them are not filled with particles. Obviously, when the SiC fibres were attached directly to the anode and therefore acted as the deposition electrode, the particles formed a coating on the fibre fabrics, which prevented any further infiltration of the gaps close to the electrode. Eventually, this effect led to the formation of inaccessible voids between the fibres, which could no longer be filled with the depositing SiC particles. This behaviour is schematically described in Fig. 6a.

To enable the deposition of SiC particles in these spaces between the fibres, the infiltration of the CNT-coated SiC-fibre mat with SiC powder was performed by placing the mat in front of the anode but not in direct contact with it, as described in our previous work.[40] As shown schematically in Fig. 6b, the fabric was attached to a cellulose membrane and was separated from the anode using a Teflon® spacer. According to a mechanism proposed elsewhere,[45] with this configuration the SiC particles are forced to move through the negatively charged fibre mat to reach the electrode; thus, they first deposit on the membrane. Next, they gradually fill the fabric in front of the membrane, and finally, the deposit is additionally formed on the front side of the fabric. The macroscopic view of the green SiC infiltrated sample, which formed in 5 min on the graphite anode at 30 V, is presented in Fig. 7a. It is evident that the particles are deposited on both sides of the SiC fibre mat, indicating that the particles were able to migrate through the fabric.

In order to verify the effectiveness of the EPD of CNTs onto SiC-fibres, and the infiltration of the CNT-coated fibre mats with SiC powder, the samples were subsequently infiltrated with an Al-phosphate solution and sintered at 1300 °C for 3 h in an argon atmosphere. The Al-phosphate provided a secondary-phase precursor that enables the low-temperature densification of SiC.[44,46] After sintering, the matrix phase filling the gaps between the CNT-coated fibres is composed of SiC particles embedded in an aluminium-containing secondary phase. The EDS spectrum of the SiC-based matrix material is presented in Fig. 7d.

The fracture surfaces of the composite illustrated in Fig. 7c and e reveal that even the narrow spaces between the fibres are filled with the SiC matrix, as desired. A few unfilled gaps still remain, however, which could be addressed by a further improvement of the process. Moreover, from the higher magnification image in Fig. 7f, it is evident that the CNT-coating is still present on the fibres after the high-temperature treatment.

4. Conclusions

The aim of the work was to produce a new grade of CNT-coated SiC-fibres-reinforced SiC-composite by using electric-field-assisted processes for the coating and infiltration. This was done in two steps: firstly, the SiC fibres were coated by CNTs and, secondly, the coated fabric was infiltrated with a SiC-powder suspension.

High-quality, uniform, and reproducible CNT and CNT-SiC coatings on SiC fibres were produced for the first time using the EPD technique and aqueous suspensions. Since the SiC fibres were shown to be negatively charged within a wide range of pH values, we used negatively charged CNTs and SiC particles for the EPD experiments. Steel, copper, and graphite electrodes were employed. Using steel electrodes at voltages greater than 2.8 V, meant bubbles disturbed the deposition, while using copper and graphite deposition electrodes successfully suppressed the bubbles' formation, which is a requisite for the formation of solid pore-free deposits.

In the electrophoretic deposition of CNTs onto SiC fibres in contact with the positive electrode, a continuous layer of CNTs was formed on the fibres. The subsequent deposition of the SiC particles on the CNT-coated fibres yielded a thick SiC layer on SiC fibres; however, the spaces between the fibres through the thickness of the fibre mat were not completely filled and the infiltration of the fibre mat was not achieved. A more efficient infiltration of the CNT-coated SiC fibres was achieved by placing the fibres close to the anode, but not in direct contact with it. In this way the particles migrated to the electrode through the fibre mat and gradually filled it.

We demonstrated that EPD is a highly efficient method to coat SiC fibres with a layer of CNTs, which results in a nanostructured interphase layer in the SiC-fibre-reinforced SiC ceramics. Future work will determine whether or not the presence of CNT coating will lead to enhanced thermal conductivity and fracture toughness of these composite materials.

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